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JOURNAL OF SCIENCE.

CONDUCTED BY

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AND

WILLIAM FRANCIS, F.L.S.

12

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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes." Just. Lips. *Polit.* lib. i. cap. 1. Not.

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VOL. XXII.—SIXTH SERIES.

JULY—DECEMBER 1911.

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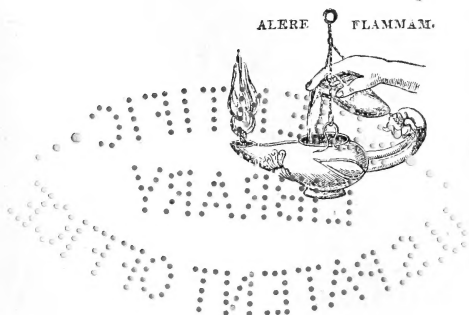
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“Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem.”—*Hugo de S. Victore.*

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—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condant,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*



# CONTENTS OF VOL. XXII.

(SIXTH SERIES).

NUMBER CXXVII.—JULY 1911.

	Page
Sir Oliver Lodge on the Mode of Conduction in Gases illustrated by the Behaviour of Electric Vacuum Valves ..	1
Dr. A. S. Eve on the Coefficient of Absorption by Air of the Beta Rays from Radium C .....	8
Mr. W. Sutherland on Weak Electrolytes and towards a Dynamical Theory of Solutions .....	17
Mr. S. B. McLaren on the Emission and Absorption of Energy by Electrons .....	66
Dr. J. E. Mills on the Relation of Temperature and Molecular Attraction .....	84
Mr. G. H. Berry on Pianoforte Bridges. (Plate I.) .....	113
Prof. C. Barus on Elliptic and other Interference with Reflecting Gratings .....	118
Lord Rayleigh on Aberration in a Dispersive Medium.....	130
Prof. J. Joly on a Method of Investigating the Quantity of Radium in Rocks and Minerals, &c. ....	134
Dr. W. F. G. Swann on the Magnetic Field produced by a Charged Condenser moving through Space .....	150
Mr. G. H. Livens on the Initial Accelerated Motion of a Rigidly Charged Dielectric Sphere .....	169
Mr. L. R. Manlove: Proposed Method for the better practical Application of Fourier's Theorem concerning the Roots of an Algebraical Equation .....	173
Prof. D. N. Mallik on Lines of Force due to given Static Charges. (Plate II.) .....	177
Mr. R. F. Gwyther on the Stresses in a Heavy Spherical Shell .....	191
Dr. W. C. McC. Lewis on the Internal Pressure of a Liquid.	193
Mr. E. C. Snow: Note on the Paper by Prof. Rutherford, F.R.S., and H. Geiger, Ph.D., on "The Probability Variations in Distribution of $\alpha$ Particles" .....	198
Dr. H. Geiger on the Transformation of the Actinium Emanation .....	201
Prof. J. S. Townsend on Charges on Ions in Gases .....	204
The Earl of Berkeley and Dr. C. V. Burton on a Thermostat for Controlling the Temperature of a Room .....	211
Dr. F. Horton on the Origin of Spectra .....	214

	Page
Notices respecting New Books:—	
Publications of the U.S. Coast and Geodetic Survey ..	219
Proceedings of the Geological Society:—	
Mr. R. L. Sherlock on the Relationship of the Permian to the Trias in Nottinghamshire.....	220
Intelligence and Miscellaneous Articles:—	
On the Equation of Continuity of the Liquid and Gaseous States of Matter, by A. Batschinski .....	221
The Principle of Relativity, by E. M. Lémeray .....	222
The Mode of Ionization by X-Rays, by Prof. W. H. Bragg.	222
Correction to his Paper on the "Longitudinal and Trans- verse Mass of an Electron," by W. F. G. Swann ...	223
Annual Tables of Constants and Numerical Data .....	223

---

### NUMBER CXXVIII.—AUGUST.

Lord Rayleigh on the Calculation of Chladni's Figures for a Square Plate.....	225
Prof. L. P. Wheeler: An Experimental Investigation on the Reflexion of Light at certain Metal-Liquid Surfaces ....	229
Dr. J. W. Nicholson on the Number of Electrons concerned in Metallic Conduction .....	245
Dr. J. W. Nicholson on the Optical Properties of Fused Metals .....	266
Dr. W. C. McC. Lewis on the Latent Heat of Vaporization of Liquids .....	268
Mr. Norman Campbell on Delta Rays .....	276
Mr. Andrew Stephenson on Absorption and Dispersion ....	303
Mr. R. B. Sangster: Some Consequences of Fresnel's Reflexion of Light Theory, with Formulæ for Determining the Angle of Incidence in order to reflect $1/n$ th the Incident Light..	305
Prof. H. du Bois and Prof. H. Rubens on Polarization of Undiffracted Long-waved Heat Rays by Wire Gratings ..	322
Mr. G. F. Becker on some New Mechanical Quadratures ..	342
Mr. A. J. Lotka on the Ratios which the Amounts of Substances in Radioactive Equilibrium bear to one another.	353
Notices respecting New Books:—	
Bulletin of the Bureau of Standards .....	354
U.S. Coast and Geodetic Survey: Directions for Magnetic Measurements by D. L. Hazard .....	355
Intelligence and Miscellaneous Articles:—	
On the Laws of Molecular Attraction, by Dr. R. D. Kleeman	355

---



## NUMBER CXXIX.—SEPTEMBER.

Prof. J. Joly on the Age of the Earth. (Plate III.)	357
Lord Rayleigh: Problems in the Conduction of Heat	381
Prof. C. G. Barkla on the Spectra of the Fluorescent Röntgen Radiations	396
Mr. E. W. B. Gill on the Intensity of the Ultra-Violet Light emitted by an Electrical Discharge at Low Pressures	412
Mr. G. N. Antonoff on the Disintegration Products of Uranium	419
Mr. A. Norman Shaw on Increased Accuracy in the Use of Bifilar Suspensions	433
Dr. C. A. Sadler on the Transformation of the Energy of Homogeneous Röntgen Radiation into Energy of Corpuscular Radiation	447
Dr. R. C. Tolman: Non-Newtonian Mechanics.—The Direction of Force and Acceleration	458
Notices respecting New Books:—	
Prof. J. A. Fleming's Principles of Electric Wave Telegraphy and Telephony	463
Proceedings of the Geological Society:—	
Mr. H. H. Thomas on the Skomer Volcanic Series	465
Mr. R. H. Rastall on the Geology of the Districts of Worcester, Robertson, and Ashton (Cape Colony)	466
Mr. A. Wade on the Eastern Desert of Egypt, with Considerations bearing upon the Origin of the British Trias	467
Mr. A. Wade on the Llandovery and Associated Rocks of North-Eastern Montgomeryshire	467

## NUMBER CXXX.—OCTOBER.

Prof. R. W. Wood on the Resonance Spectra of Iodine Vapour and their Destruction by Gases of the Helium Group. (Plates IV. & V.)	469
Mr. J. Prescott on the Rigidity of the Earth	481
Dr. J. H. Vincent: Electrical Experiments with Mercury contained in Tubes. (Plates VI. & VII.)	506
Prof. Augustus Trowbridge and Mr. Irving B. Crandall on Groove-Form and Energy Distribution of Diffraction Gratings. (Plates VIII.—XI.)	534
Dr. J. Franck and Dr. W. Westphal on the Question of Valency in Gaseous Ionization	547
Dr. A. S. Eve on the Number of Ions produced by the Beta Rays and by the Gamma Rays from Radium C	551
Dr. Gwilym Owen on the Production of Nuclei in Air by Intense Cooling	563
Dr. R. D. Kleeman on Molecular Attraction and the Properties of Liquids	566

	Page
Prof. B. B. Boltwood and Prof. E. Rutherford on the Production of Helium by Radium.....	586
Dr. H. Geiger and Dr. A. F. Kovarik on the Relative Number of Ions produced by the $\beta$ Particles from the Various Radioactive Substances .....	604
Dr. H. Geiger and Mr. J. M. Nuttall on the Ranges of the $\alpha$ Particles from Various Radioactive Substances and a Relation between Range and Period of Transformation ..	613
Prof. E. Rutherford and Dr. H. Geiger: Transformation and Nomenclature of the Radioactive Emanations .....	621
Mr. H. G. J. Moseley and Dr. K. Fajans: Radio-active Products of Short Life .....	629
Prof. J. C. McLennan and Mr. E. N. Macallum on the Intensity of the Earth's Penetrating Radiation at Different Altitudes and a Secondary Radiation excited by it .....	639
Mr. J. L. Glasson on the Variation of Ionizing Power with the Velocity of Cathode Rays .....	647
Prof. J. S. Townsend and Sir Oliver Lodge on the Mode of Conduction in Gases .....	656
Mr. J. R. Airey: Tables of Neumann Functions $G_n(x)$ and $Y_n(x)$ .....	658
Prof. W. Peddie on the Problem of Partition of Energy, especially in Radiation.....	663
Mr. L. R. Manlove: Supplemental Note on a Proposed Method for the better practical application of Fourier's Theorem .....	668

---

### NUMBER CXXXI.—NOVEMBER.

Prof. O. W. Richardson on the Positive Ionization from Hot Salts .....	669
Prof. O. W. Richardson and Mr. R. C. Ditto on the Diffusion of Neon through Hot Quartz .....	704
Prof. E. Taylor Jones and Mr. D. E. Roberts on the Induction-Coil. (Plates XII. & XIII.) .....	706
Mr. H. Donaldson on the Spectra of the Electrodeless Ring Discharge in certain Gases .....	720
Mr. G. Stead on the Separation of Spectra in Compound Gases .....	727
Lord Rayleigh on the General Problem of Photographic Reproduction, with suggestions for enhancing Gradation originally invisible .....	734
Dr. R. A. Houstoun on a Relation between Tension and Torsion.	740
Dr. Henry Wilde on the Origin of Cometary Bodies and Saturn's Rings. (Plates XIV. & XV.) .....	741
Mr. H. D. Arnold: Limitations imposed by Slip and Inertia Terms upon Stokes's Law for the Motion of Spheres through Liquids .....	755

	Page
Mr. S. G. Lusby on the Mobility of the Positive Ion in Flames .....	775
Mr. G. W. Todd on the Mobility of Positive Ions produced from Heated Aluminium Phosphate in Gases at Low Pressures .....	791
Mr. H. Carter on the Radioactive Properties of High Temperature Flames .....	805
Prof. J. S. Townsend on the Mode of Conduction in Gases..	816
Notices respecting New Books:—	
Gesammelte Abhandlungen von Friedrich Kohlrausch..	819
Dr. G. T. Walker's Outlines of the Theory of Electro- magnetism .....	819
Proceedings of the Geological Society:—	
Dr. J. D. Falconer on the Geology of Northern Nigeria.	820

---

### NUMBER CXXXII.—DECEMBER.

Messrs. S. Kinoshita, S. Nishikawa, and S. Ono on the Amount of the Radioactive Products present in the Atmo- sphere .....	821
Dr. R. W. Boyle on the Solubility of Radium Emanation: Application of Henry's Law at Low Partial Pressures....	840
Mr. Otto Stuhlmann, Jr., on the Difference in the Photoelectric Effect caused by Incident and Emergent Light.—Part II..	854
Dr. J. W. Nicholson on a Structural Theory of the Chemical Elements .....	864
Prof. E. P. Adams on Electrostriction .....	889
Mr. C. W. Heaps on the Effect of Magnetic Fields on Metallic Resistance. (Plate XVI.) .....	900
Prof. H. A. Bumstead on the Emission of Electrons by Metals under the Influence of Alpha Rays .....	907
Mr. R. Rossi on a Relation between the Atomic Volumes and the Spectra of Elements .....	922
Prof. Chas. T. Knipp: Rays of Positive Electricity from the Wehnelt Cathode. (Plate XVII.) .....	926
Mr. S. A. Shorter on the Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.—Part I. ....	933
Mr. G. H. Livens on some Further Problems connected with the Motion of Charged Spheres .....	943
Dr. Henry Wilde on the Periodic Times of Saturn's Rings..	949
Notices respecting New Books:—	
Dr. E. T. Whittaker's History of the Theories of Æther and Electricity from the Age of Descartes to the close of the Nineteenth Century .....	951
Proceedings of the Geological Society:—	
Mr. R. J. Lechmere Guppy on the Geology of Antigua and other West Indian Islands .....	953
Index .....	954

## PLATES.

- I. Illustrative of Mr. G. H. Berry's Paper on Pianoforte Bridges.
  - II. Illustrative of Prof. D. N. Mallik's Paper on Lines of Force due to given Static Charges.
  - III. Illustrative of Prof. J. Joly's Paper on the Age of the Earth.
  - IV. & V. Illustrative of Prof. R. W. Wood's Paper on the Resonance Spectra of Iodine Vapour and their Destruction by Gases of the Helium Group.
  - VI. & VII. Illustrative of Dr. J. H. Vincent's Paper on Electrical Experiments with Mercury contained in Tubes.
  - VIII.-XI. Illustrative of Prof. A. Trowbridge and Mr. I. B. Crandall's Paper on Groove-Form and Energy Distribution of Diffraction Gratings.
  - XII. & XIII. Illustrative of Prof. E. Taylor Jones and Mr. D. E. Roberts's Paper on the Induction Coil.
  - XIV. & XV. Illustrative of Dr. Henry Wilde's Paper on the Origin of Cometary Bodies and Saturn's Rings.
  - XVI. Illustrative of Mr. C. W. Heaps's Paper on the Effect of Magnetic Fields on Metallic Resistance.
  - XVII. Illustrative of Prof. C. T. Knipp's Paper on Rays of Positive Electricity from the Wehnelt Cathode.
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## ERRATA.

- Page 175, line 4 from bottom, *for*  $F_A(u_1)$  *read*  $F_A(u_1)=0$ .
- Page 534, line 5, *for* [Plates VIII.-X.] *read* [Plates VIII.-XI.]
- Page 543, line 1, *for* Pl. IX. *read* Pl. XI.

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[SIXTH SERIES.]

JULY 1911.

- I. *The Mode of Conduction in Gases illustrated by the Behaviour of Electric Vacuum Valves.* By SIR OLIVER LODGE\*.

ASSISTED by Mr. E. E. Robinson, I have during the past few years made many experiments in connexion with electric vacuum valves, and have arrived at a view or theory concerning their action which may be worth setting down with as much brevity as is consistent with clearness.

The main points to bear in mind are three:—

- (1) One is that the current in vacuum-tubes is mostly conveyed unobtrusively by positively charged carriers or atoms, which travel from anode to cathode as best they can,—readily taking a roundabout path if necessary, *i. e.* if any serious obstruction exists in a more direct path.
- (2) The second point is quite familiar, and is that from the surface of the cathode a bombardment of negative corpuscles or electrons occurs from every place at adequate tension, and issues everywhere perpendicular to the surface without regard to destination.

At high vacua these projectiles travel with prodigious speed for a considerable distance, and they have the effect of blocking the path by driving back any small bodies such as atoms advancing in an opposite direction.

\* Communicated by the Author.

## 2 Sir Oliver Lodge on the Mode of Conduction in Gases

The negatively-charged projectiles carry only an insignificant proportion of the whole current, though they may assist in propelling uncharged atoms towards the anode, where they can become positive ions.

- (3) The third point essential to an explanation is that circulation of material in the tube is necessary, so as to maintain a constant supply of positively charged ions, and to enable them to act as carriers.

This last statement needs expansion :—

However plentifully electrons are supplied to the cathode by the source of current, they do not spontaneously escape from the metal (except under some stimulus such as ultra-violet light provides) unless positively charged ions are in their neighbourhood, *i. e.* unless the tension  $2\pi\sigma^2$  rises to a critical value.

In an active vacuum-tube the continual presence of such ions near the cathode depends on their having been able to travel from the anode ; nevertheless they are not atoms of the anode itself, but are gas atoms which have become positively charged by contact with it,—each of them having presumably given up an electron to the metal.

It is at the surface of the anode therefore that the separation of electricities really takes place, under stress of the applied E.M.F. The ions then migrate to the cathode, and extract from it an electron apiece, thereby becoming neutral again.

A constant diffusion of uncharged atoms towards the anode and of positively charged ions away from it is therefore essential to the passage of current. The cathode bombardment roused by the presence of the advancing ions can be so planned or directed as to assist or to oppose the necessary circulation. The projectiles may assist by mechanically propelling uncharged atoms towards the anode, or they may oppose by mechanically driving back charged ions which are trying to advance away from it.

In doing the latter it would seem as if they ought to neutralize opposing charges and thus convey some current ; but the evidence points to the supposition that such flying neutralization is rare,—it either does not occur or is but a small fraction of the whole. The impacts shake, but perhaps do not electrify or discharge, the ions : most of the interchange of electricity seems to go on only at or close to the metal surfaces.

If now a cathode is mounted so as to fire down a narrow tube along which the positive carriers must come, it acts like a park of Maxim guns obstructing a troop of infantry ; and



the passage of the current is rendered impossible, unless some supplementary—some tortuous or indirect route is provided, whereby a stream of positive carriers can reach the cathode after travelling through a region in which the bombardment is less vigorous.

The general direction of the whole bombardment depends on the shape and aspect of the cathode. From all flat surfaces it must be intense and in nearly parallel lines; from a concave surface it is well known to concentrate to a focus; from a convex surface it is divergent, and therefore feebler; and from a very convex surface, like an edge or still more a point, it is distributed in so many directions that part of the opposite procession of heavy atoms has a chance of eluding the projectiles.

Consequently to any edge or point of the cathode positive charges may be seen streaming in; evidence of the stream being a local manifestation of the colour due to the chemical nature of the gas, owing to a certain percentage of the atoms being struck as they come along in the teeth of the diffuse bombardment. It would appear that uncharged atoms, even if struck, do not glow perceptibly. Perhaps because they are all driven out of the field—the region of the dark space—at once.

If the cathode contains a hollow space into which the positive carriers can find their way, this space becomes filled with the chemical glow,—*i. e.* the glow characteristic of the chemical nature of the gas,—which is presumably caused by radiation from its positively charged atoms when they are struck by the flying electrons.

If the cathode is a long cylinder or wire, the lateral radiation is sufficiently diffuse to allow some obstructed access to its curved surface; and if the wire is coiled up into a spiral, access is much easier, for then the space in the interior of the spiral becomes practically a hollow space into which some of the positive carriers contrive to enter and rest till they have lost their charges.

But if the cathode is made spherical and quite smooth, it must be extremely difficult for the positive carriers to find any means of access. Still more difficult will it be if the cathode is a small flat surface at the mouth of a narrow tube so arranged as to furnish the only means of approach.

A cathode shaped like a tetrahedron or triangular pyramid with its edges not completely closed (made by folding over the corners of an equilateral triangle and leaving millimetre chinks) is an instructive shape. To each point of the pyramid the positive stream is seen going, because thence

the projectiles radiate divergently so that they become places of minimum bombardment; while the interior hollow space is filled with light,—the carriers there delivering up their charges, or remaining long enough to have it bombarded out of them by the electrons.

A “valve” is a contrivance which permits the passage of electricity in one direction only, or at least very much more readily in one direction than the opposite. The special feature or desideratum of anything which is to act as a valve, therefore, is to have one terminal situated so that it can fire down a constricted space and stop any procession coming along it, while the other terminal should be in a roomy chamber; moreover this latter terminal should have points or edges whence the bombardment will be diffuse. It may likewise have interstices or hollow spaces wherein the bombardment, apart from the presence of positive carriers, would be either weak or non-existent. It should have no part of its surface arranged so as to fire down the tube leading to the other terminal, but free and open means of access should be provided in every direction. In other words, one terminal should be near the centre of a large bulb, while the other terminal is in a narrow tube.

With such an arrangement the constricted terminal can easily act as anode and supply the current to the other one; but if it is made to act as cathode, its cannonading activity stops the advancing carriers and checks the current almost entirely. It will also heat and crack the glass unless suitable precautions are taken.

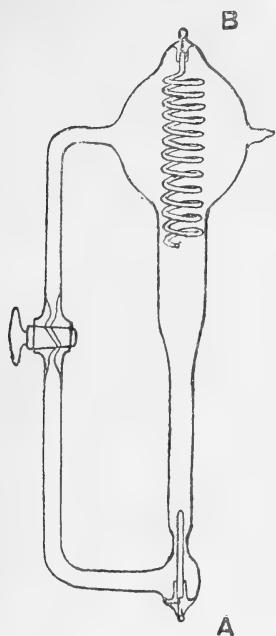
Although it is thus easy to understand the principle upon which valves are based, it is not at all easy to construct them so that they shall work well and permanently; many things may go wrong, and a good deal of experience is needed for their manufacture and right exhaustion. Every valve ought to be tested and adjusted, if it is to be satisfactory. At present they are made for me by Mr. Cossor in London and tested in my laboratory.

#### *Illustrative Experiment.*

Selected out of a great number of experiments, the following sample may serve compactly to illustrate the principles here laid down:—

A tube was made in accordance with the drawing, a supplemental path being provided with a tap, the terminals being A and B; and with it the following tests were made—

1. With the tap closed, so that nothing could pass by the supplementary path, A was made negative and B positive.



Cathode rays are then given off strongly from the end of the rod A and make the glass glow up to about where the tube above widens. They excite phosphorescence also up at the top near B. There are practically no cathode rays from any other part of the rod A, and there are none in the small bulb round it. Hardly any positive glow is visible, and the resistance of the tube, thus connected, is very high.

2. The connexions were reversed, so that A was positive and B negative ; the tap being still shut.

Strong cathode rays now emanate from the bottom end of the spiral, heating the glass there vigorously and threatening to destroy it ; but there are no cathode rays in the bulb above, outside the spiral, showing that they do not start in all directions without regard to where positive charges can be found. It is well known that they do not pay any attention to the position of the anode, but they do to the position of the positive carriers.

There was little or no luminous glow, apart from the phosphorescence of the glass, in either of these two first cases, *i. e.* with the tube shut.

3. Next test. The tap was opened so as to enable the current to pass by the supplementary path. If now A is made negative and B positive, cathode rays emanate from all parts of the rod A and drive along both the vertical and the horizontal tube. The resistance at high vacuum is therefore very great, and there is practically no positive glow visible.

4. The connexions were now reversed, so that A was positive and B negative. Cathode rays are now manifest and plentiful in the bulb outside the spiral, whereas few or none are perceived at the bottom of the spiral, and no strain is there noticeable. In fact everything is easy, and there is very little heating effect. The luminous glow is strong in the vertical part of the tube between the rod A and the spiral, and inside the spiral: it is also visible, though rather weak, along the supplementary path. The resistance of the tube thus arranged is low, it conveys a considerable current easily. It is in fact evident that the main current travels upward fairly freely from rod A; the bombardment opposed to it being considerably relieved by the fact that negative projectiles from the sides of the spiral are now possible, owing to the positive carriers which come along the supplementary path in sufficient quantity. The constant supply of such positive carriers is presumably assisted by the driving down of neutral atoms towards the anode, whence they can pass through the constricted space round it, can enter the little bulb and so make their way up the supplemental path through the tap, as required.

#### *Comment.*

If it be asked how it happens that the bombarding electrons convey so little current, though their mechanical effort is so energetic, the first answer that suggests itself is that it is because their velocity is so high, approximating to the order of the velocity of light. The slow moving positive charges would seem likely to have but little kinetic energy, though they can convey much current; the quickly flying electrons would be in the opposite plight.

The mechanical energy depends upon  $nmu^2$ , the current conveying capacity upon  $neu$ . Hence sufficient carriers at low speed would be effective conveyers of current, though without energy enough to progress in the teeth of projectiles moving at anything like the velocity of light.

But considering the matter further, it can be argued that the positive carriers must sooner or later be all neutralized by meeting an electron; wherefore in the last resort the total

carrying power of positive and negative ions will be equal : that is to say,  $neu$  will be the same for both. And, since  $e$  is undoubtedly the same for both, this means that  $nu = NU$ , while the ratio of their aggregate energies,  $\frac{nmv^2}{NMU^2} = \frac{nu}{MU}$ , is the same as the ratio of their individual momenta.

If the same propelling force acts on both sets for the same time, it may be supposed that the individual momenta are equal. If so,  $\frac{n}{N} = \frac{U}{u} = \frac{m}{M}$ .

Now if the gas be (say) nitrogen, the ratio of the mass of an atom to that of an electron is  $M/m = 14 \times 1700 = 23,800$ ; or the speed of the atoms is less than the twenty thousandth of that of the electrons, though they are more than twenty thousand times as numerous.

But though the individual momenta of opposing bodies—electrons and atoms—are equal, so that they can stop each other on collision, it is plain that the *aggregate* electronic momentum is the smaller of the two, and that matters can be so arranged that a large part of it can be absorbed close to the cathode, or can be coaxed into regions, such as the interior of hollow spaces, where its violence will be mechanically inoperative, while a fairly unobstructed path is left to the effective carriers; and this is what is arranged in an easy tube, or in the easy direction of a valve.

Although the positive carriers are spoken of as comparatively leisurely, it is not to be supposed that they are what in ordinary speech is called “slow.” Their speed appears to be of the order of a kilometre per second.

#### General Remarks.

Incidentally it may be worth explicitly noting that whereas in vacuum-tubes the positively-charged atoms are the main conveyers of the current, in metals the conduction is almost certainly due to the free migration of electrons; while in liquid electrolytes the conduction is distributed in approximately equal proportions, or rather in perfectly known numerical proportions, between the positive and negative ions.

The fact that the conveyers of electricity have to change in sign when a current passes from a metal to a gas, or *vice versa*, which exchange can only be effected by a neutralization or combination of the opposite charges at the bounding surface, suffices to account for some of the heat which is there developed.

University of Birmingham.

II. *On the Coefficient of Absorption by Air of the Beta Rays from Radium C.* By A. S. EVE, M.A., D.Sc., McGill University, Montreal\*.

THE object of this paper is to describe a new method of finding the value of  $\mu$  the coefficient of absorption of the  $\beta$  rays from radium C in their passage through air at atmospheric pressure and at room temperature; and to give the value of  $\mu$  obtained in a series of experiments.

The general method employed is simple. A very thin-walled electroscope was suspended by fine wires at a considerable distance from surrounding objects. A test-tube containing radium bromide was also suspended at various distances from the electroscope. The ionization current in the electroscope, measured in divisions per minute of the observing microscope, was due to the joint effects of the  $\beta$  rays,  $\gamma$  rays, and natural leak. The  $\beta$  rays were then cut off by screens, or by a strong magnetic field, or, better still, by both methods, and the ionization due to  $\gamma$  rays and natural leak measured. As the natural leak is known, by subtraction measurements are obtained of the ionization due to the  $\beta$  rays alone,  $I$ , and to the  $\gamma$  rays alone,  $I'$ .

As the distance  $r$  between the radium and electroscope is increased, the value of  $I$  falls off sharply, not only on account of the law of inverse squares, but also on account of the absorption by air of the complex  $\beta$  rays of radium C which, as these experiments will show, obey closely the exponential law. Thus we shall see that the experiments justify the assumption that the ionization in the electroscope  $I$  varies inversely as  $r^2 e^{\mu r}$  or

$$Ir^2 = Ae^{-\mu r},$$

where  $A$  is a constant, and  $\mu$  is the coefficient of absorption by air.

If the ionization current, multiplied by the square of the distance, is plotted against the distance, an exponential curve is determined. Or, on taking logarithms,

$$\log_e Ir^2 = B - \mu r,$$

and when this is plotted with  $\log_e Ir^2$  as ordinate, and  $r$  as abscissa, a straight line is determined, whose slope is  $\mu$ .

It will be observed that the multiplication by  $r^2$  is equivalent to a handicap for loss of distance.

\* Communicated by the Author.

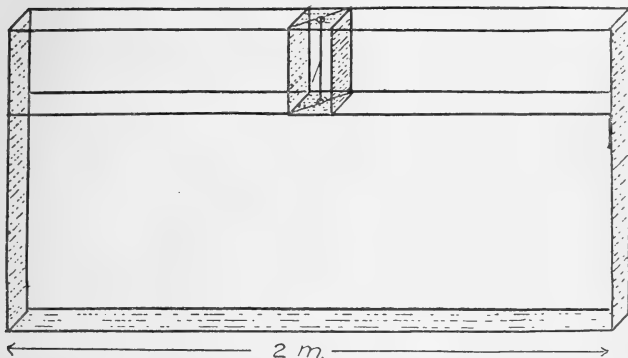


A similar process for the ionization due to the  $\gamma$  rays gives  $I/r^2$  a constant, because of the minute absorption which the  $\gamma$  rays undergo, over a range of a few metres in air.

*Electroscopes.*

One electroscope ( $20 \times 10 \times 10$  cm.), fig. 1, was built of a

Fig. 1.



framework of light steel knitting-needles. This was covered with tissue-paper, blackened inside with pencil, weighing  $\cdot 002$  gram to the square centimetre, so that the stopping power of the wall was less than that of 2 cm. of air. The framework was suspended, and held firmly by light steel wires to a wooden frame near the middle of the room, well removed from other bodies. The observer approached the electroscope only for a few seconds at the beginning and towards the end of a reading. The microscope could be similarly removed and replaced, but this proved to be unnecessary as the correction was negligible. The mica windows were exceedingly thin, and the light aluminium leaf system was charged through a trap-door in the paper. Considerable variation in the natural leak occurred at first, and was traced to daylight entering the tissue-paper, and making the sulphur insulator a partial conductor. This trouble was obviated by working in a darkened room, and subsequently by using amber insulators. The effect of daylight on sulphur was first discovered by Bates of Macdonald College, and it has been suggested that sulphur shares to a small degree the well-known property of selenium. In the usual thick-walled electroscope the effect is slight, and may escape notice.

Another electroscope consisted of a framework of thin knitting-needles mounted on tall light wooden pillars. In

this case the framework was covered with aluminium leaf  $\cdot 0003$  cm. thick, weighing about  $\cdot 0008$  gram to the square centimetre, with a stopping power of about 7 mm. of air. It is easily shown by experiment that when the walls are covered with two or three times this thickness of aluminium leaf, neither the  $\beta$  nor the  $\gamma$  ray ionizations are altered to an extent which can be detected.

Thus the experimental conditions ensure the desired result, that is, the investigation of an elementary volume of air, practically removed from any important modification due to reflected or scattered or secondary radiation from surrounding bodies, excepting the air and radiating source.

### *Long Range Experiments.*

It was found possible to detect the direct  $\beta$  radiation from 14.6 mg. of pure radium bromide (8.5 mg. of radium) placed within two test-tubes, at a distance of 7 metres, and to make fairly accurate measurements at 6 metres. The test-tubes reduced the  $\beta$  radiation from radium C to about half value, and the radiation from radium B was negligible.

A single experiment may be given in detail where the ionization from  $\beta$  and  $\gamma$  rays together was measured at ranges from 1 to 6 metres. The  $\beta$  rays were then cut off to a great extent by two sheets of aluminium, each 1.7 mm. thick, placed at the radium. These would permit about one per cent. of  $\beta$  rays to pass through them, and would reduce the  $\gamma$  radiation by about two per cent.

After deducting the natural leak, the readings in divisions per minute were taken and the results obtained are as follows, where I is the ionization due to  $\beta$  rays, and I' to  $\gamma$  rays:—

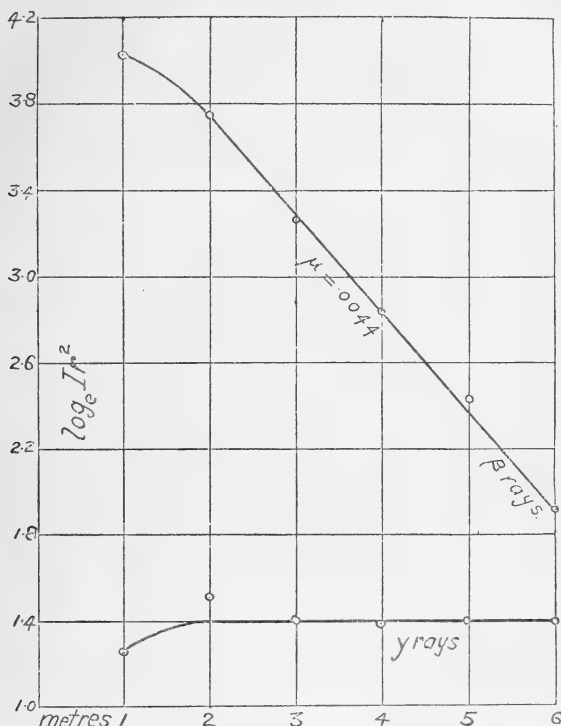
TABLE I.

Metres.	I+I'.	I'.	I' $\gamma^2$ .	I.	$\log_e I\gamma^2$ .	$\mu$ .
1	69	12.5	12.5	56.5	4.03	$\cdot 0029$ $\cdot 0048$ $\cdot 0042$ $\cdot 0041$ $\cdot 0051$
2	14.3	3.78	15.1	10.52	3.74	
3	4.47	1.57	14.1	2.90	3.26	
4	1.94	.87	13.9	1.07	2.84	
5	1.02	.57	14.1	.45	2.43	
6	.58	.39	14.0	.19	1.92	

$$\mu = \cdot 0044 \text{ cm.}^{-1}$$

These results are also shown in fig. 2, where the abscissæ are given in metres and the ordinates are the logarithms

Fig. 2.



of  $I$  in divisions for one minute, multiplied by the distance squared in metres. The upper curve represents the  $\beta$  ray measurements. At one metre the ordinate appears to be too small, possibly because of insufficient voltage to secure saturation, or because of some other effect requiring a special investigation. The average slope for distances most favourable to accurate measurements gives  $\mu = 0.044 \text{ cm.}^{-1}$

The lower curve is for  $\gamma$  rays, and a straight line is anticipated. The initial rise is not easy to explain; the point at 2 metres is too high owing to accidental conditions. In this experiment it is certain that some  $\beta$  particles passed through the aluminium screens, and that others were produced by the  $\gamma$  rays at emergence from the screens near the radium.

Therefore, some experiments were made in which the

test-tube containing the radium was placed inside a cylinder of zinc between the poles of a powerful electromagnet, and the magnetic field was increased in strength until the  $\beta$  radiation was eliminated. After measuring the ionization due to the  $\gamma$  rays, the electromagnet was run back, the zinc cylinder removed, and the joint  $\beta$  and  $\gamma$  ionizations determined.

It is difficult to remove the  $\beta$  radiation by screens alone, or by a powerful magnetic field alone, but a combination of screens and field is very effective.

The values of  $\mu$  found for distances from 2 to 5 metres, under various conditions, were as follows:—

$$4.4, 4.5, 3.9, 5.0; \text{ cm.}^{-1} \times 10^3,$$

and the mean value was  $\mu = .0045 \text{ cm.}^{-1}$

Eleven milligrams of radium bromide in solution in a thick-walled glass bottle emitted some  $\beta$  radiation, which could be screened off by aluminium and zinc sheets placed near the bottle. The values of  $\mu$  for these  $\beta$  rays were:—

$$\begin{array}{l} \text{distance 1 to 2 metres } \mu = .00385, \\ \text{,, } 2 \text{ ,, } 3 \text{ ,, } \mu = .0041, \\ \text{Mean } \mu = .0040 \text{ cm.}^{-1} \end{array}$$

It is concluded that for absorption at distances from  $r=2$  to  $r=5$  metres the value of  $\mu$  is approximately  $.0045 \text{ cm.}^{-1}$ .

### *Short Ranges.*

Some weaker specimens of radium were next tested at shorter distances. The specimens chiefly used were, (1) a capsule with a thin mica cover containing 0.56 mg. of radium bromide (0.33 mg. of radium), and (2) some radium bromide in a thin-walled small glass tube, containing .53 mg. of radium, the preparation being at about one-quarter of full strength. The latter specimen was kindly lent to me by Professor H. A. Wilson.

The radium tube was hung by a thread at distances varying from 40 to 160 cm. from the electroscope, and readings were taken both when advancing and retiring the radium. When measuring the joint  $\beta$  and  $\gamma$  ionization, it was necessary to withdraw the large and massive electromagnet to a distance, otherwise the effect of "reflected" radiation was strongly marked. The  $\beta$  rays were then cut off by screens and a strong field, and the ionization due to

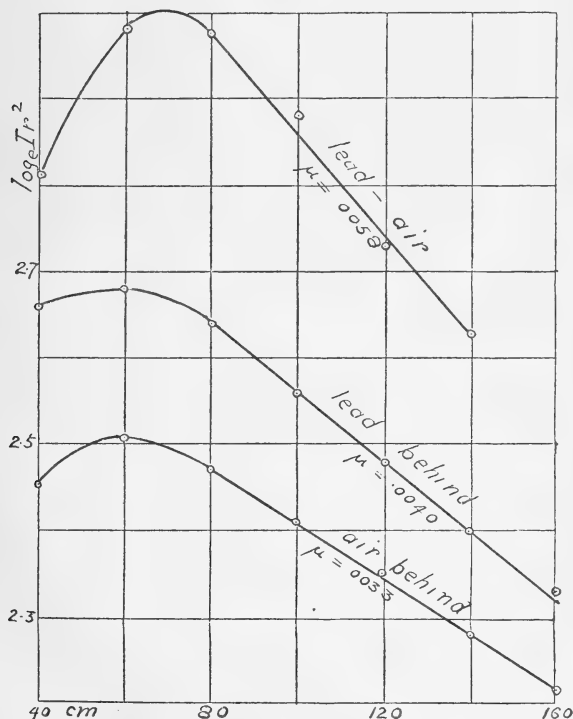
$\gamma$  rays alone was determined. It has been shown by Schmidt, and by Kovarik, that the value of  $\mu$  is affected by the material behind the radioactive source. The experiments may be divided into two series: those in which there was air, or carbon, or solid paraffin behind the radium tube, and those in which lead plates were placed behind. The values for  $\mu$  in  $\text{cm.}^{-1} \times 10^4$  were:—

Air behind .....	33, 33, 31.	Paraffin behind...	35, 38.
Carbon behind...	31.	Lead behind .....	37, 37, 40.

As  $r$  increases from 60 to 140 cm. the value of  $\mu$  is about  $\cdot 0033$  with air behind, and about  $\cdot 0038$  with lead behind.

In fig. 3 are shown graphically the results of two typical series of experiments with air and with lead behind the tube of radium.

Fig. 3.



The "reflected" radiation from lead can be determined by subtraction, and on multiplying by the square of the

distance and taking logarithms for ordinates, a curve is obtained indicating the difference between two exponentials. The straighter portion gives a value of  $\mu = 0.0058 \text{ cm.}^{-1}$ . In some cases the lead reflexion increased the ionization 88 per cent., and copper 64 per cent. We may compare the results of Kovarik, when aluminium absorbed the  $\beta$  rays from radium E, namely :—

air behind.....	$\mu = 42.4 \text{ cm.}^{-1}$
lead „ .....	$\mu = 44.8 \text{ „}$
lead minus air.	$\mu = 51.0 \text{ „}$

#### Discussion.

So far as I am aware, no previous measurements have been made of the value of the coefficient of absorption of  $\beta$  rays in air.

Rutherford\* has given an estimate for the value for the  $\beta$  rays from uranium, namely, 0.0066. This is based on the value of  $\mu/\text{density}$ , for various metal sheets, which is about 5. It is not surprising that my value for air is less than this, since  $\mu/D$  decreases with  $D$ ; thus, for lead 10, silver 7, aluminium 5. My value for  $\mu/D$  for air is between 2.6 and 3.4, according to the experimental conditions.

It is remarkable and contrary to expectation, that the above described experiments give  $\mu = 0.0033$  for short ranges and  $\mu = 0.0048$  for long ranges. With metal screens the reverse order is usually observed, the less penetrating rays are first absorbed, and then  $\mu$  decreases for the more penetrating rays. Moreover, in the present case it is possible that some of the  $\beta$  rays of radium D at the shorter distance may reach the electroscope. Some large values of  $\mu$  found with the capsule, not recorded here, may find their true explanation in this fact.

Two different causes may be suggested to account for the paradox.

Either the  $\beta$  rays ionize more efficiently towards the end of their path when their velocities have been somewhat reduced; or at the longer ranges the scattering of the particles by air has caused the distances, which were measured on the straight, to be largely in defect of the actual total distances traversed by the electrons in their zigzag flights.

The first explanation suggests a relative increase of  $I$  at the longer ranges, due to increased ionization of lower speed  $\beta$  particles. The second explanation suggests that any

\* 'Radioactivity,' p. 197.



point on the curve should have its abscissa  $r$  multiplied by some function of  $r$ ,  $f(r)$ , which increases with  $r$ ; whilst the corresponding ordinate should have added to it  $2 \log_e f(r)$ .

Without entering further into these obscure points, it may be stated that the curves and values obtained represent the facts and results usually most required, and that the  $\beta$  rays are absorbed by a law almost exponential, but with  $\mu$  increasing, probably gradually from  $\cdot 0033 \text{ cm.}^{-1}$  to  $\cdot 0045 \text{ cm.}^{-1}$ , as  $r$  increases from 60 to 600 cm.

If a mean  $\cdot 004$  is selected, it is possible to estimate the value of the coefficient of absorption  $\mu'$  by air of the  $\gamma$  rays from radium C.

Thus for aluminium, with  $\beta$  rays from radium C, Kovarik \* finds  $\mu = 13 \text{ cm.}^{-1}$ , and with  $\gamma$  rays McClelland finds  $\mu' = \cdot 103$ . If it is assumed that the same proportion holds for  $\beta$  and for  $\gamma$  rays in passing through air, it follows that

$$\mu' / \cdot 004 = \cdot 103 / 13,$$

$$\text{so} \quad \mu' = \cdot 000032.$$

This is less than the result obtained from the value of  $\mu'/D$  found by McClelland †, namely,  $\cdot 034$ , which leads to a value

$$\mu' = \cdot 000044.$$

Soddy and Russell's ‡ value for  $\mu'/D$  gives a still larger result, so that until further light is obtained, the intermediate value  $\cdot 000044$  may be adopted.

Just as when the radioactive constant is  $\lambda$ , the average life is  $1/\lambda$ , so we may say that when the coefficient of absorption is  $\mu$ , the average distance reached is  $1/\mu$ . But it will be remembered that the distance is measured "as the crow flies," whilst the actual path is zigzag.

If in a parallel pencil of  $\beta$  rays,  $N_0$  electrons start their flight, then at a distance  $x$ , only  $N$  remain effective for ionization, so that  $-dN$  have a range between  $x$  and  $x + dx$ .

Hence

$$\frac{\int_{N_0}^0 -x dN}{N_0}$$

is the average distance attained from the source.

\* Phil. Mag. Nov. 1910.

† Phil. Mag. Aug. 1904.

‡ Phil. Mag. Oct. 1909.

## 16 *Absorption by Air of the Beta Rays from Radium C.*

It follows that the average range is the area below the curve, divided by  $N_0$ , or

$$\int N dx / N_0 = \int e^{-\mu x} dx = 1/\mu.$$

Thus, the  $\beta$  particles reached an average distance from the source in air =  $1/004$ , or 2.5 metres.

If it is correct to regard a  $\gamma$  ray as an entity, with a linear path, then its average range is the inverse of  $\cdot00004$ , or 250 metres.

If the  $\beta$  rays were ejected all with the same velocity, the above statement would have a conciseness which is lacking in the case of the complex rays from radium C.

The writer proposes to employ the method above described to determine the value of  $\mu$  for the  $\beta$  rays from radium E, and for Röntgen rays.

### *Summary.*

1. By varying the distance  $r$  between some radium and a thin-walled electroscope, the law of absorption by air of the complex rays from radium C has been established as approximately exponential.

2. If  $I$  is the ionization due to  $\beta$  rays in the electroscope at a distance  $r$  from the radium, then  $I r^2$  varies as  $e^{-\mu r}$  nearly, where  $\mu$  is the coefficient of absorption by air of the  $\beta$  rays.

3. The values of  $\mu$  have been found as  $\cdot0033 \text{ cm.}^{-1}$  at the shorter range 60 to 160 cm., and  $\cdot0045$  at longer ranges 2 to 5 cm.

4. If air absorbs  $\beta$  and  $\gamma$  rays respectively in the same proportion as does aluminium, the coefficient of absorption of the  $\gamma$  rays by air is between  $\cdot000021$  and  $\cdot000031$ .

5. With limitations, the average effective range of the  $\beta$  rays from their source may be stated as 2.5 metres. In the same sense, the average path of the  $\gamma$  rays is 250 metres, if the  $\gamma$  rays consist of entities with linear paths.

April, 1911.

### *Note added May, 1911.*

Measurements have recently been made to determine the value of  $\mu$ , when  $\beta$  rays, from the active deposit of radium on thin aluminium foil, pass to a thin-walled electroscope through air. The method employed was that given above, and the range was from 40 to 100 cm. The values of  $\mu$  found in a number of experiments were from  $\cdot012$  to  $\cdot013$ , about three or four times as large as when radium in a glass tube

was employed at longer ranges. The explanation appeared at first to be simple, and the increased value of  $\mu$  was attributed to the  $\beta$  rays from radium B. I found, however, that this large value of the coefficient of absorption persisted from 14 to 90 minutes after the thin foil was removed from the radium emanation, during which time the proportion of radium C to radium B was increasing. This point requires special investigation, but at present it appears that radium C emits a considerable proportion of slow  $\beta$  rays, comparable to those from radium B.

The active deposit of thorium was examined for distances from 20 to 30 cm. from the centre of the electroscope. In this case the  $\beta$  rays from Th A and Th D pass into and through the electroscope. The value of  $\mu$  for air was between  $\cdot 024$  and  $\cdot 025$ , but the intensity of the radiation at my disposal was insufficient for a good determination, and further measurements are in progress.

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### III. *On Weak Electrolytes and towards a Dynamical Theory of Solutions.* By WILLIAM SUTHERLAND\*.

THE chief defect of the prevalent theory of solutions is its want of a dynamical foundation. This can be completely removed only when we have a kinetic theory of liquids as adequate as the kinetic theory of gases. Meanwhile the valuable inductions associated with the names of Arrhenius, Ostwald, van't Hoff, and others are interpreted by the simplest chemical theory that will explain them, the manifest physical difficulties being simply ignored. Hence has arisen the critical attitude of physicists like Kelvin and Helmholtz towards the working hypotheses of a large part of theoretical physical chemistry. Take for instance the principle of partial ionization as applied to the simplest case of a binary electrolyte like NaCl in water. It is assumed that the degree of ionization is controlled entirely by the law of mass action, the ionizing force of the water and the electrical attractions of the oppositely charged ions for one another being completely ignored. One result of this method of proceeding is to reach a theoretical conclusion which is not verified for a typical electrolyte like NaCl. Another result, however, is to find the theoretical conclusion beautifully verified in the case of electrolytes like acetic acid. The expounders of the prevalent theories of physical

\* Communicated by the Author.

chemistry fix attention on this successful verification, and proceed to discuss the whole of electrolysis and related phenomena as if ionization were ordinary dissociation uncomplicated with any electrical phenomenon. I have sought to show in "Ionization in Solutions and Two New Types of Viscosity" (Phil. Mag. [6] xiv. p. 1, 1907) that with ordinary electrolytes the ionizing action of the solvent is so powerful that it holds the tendency of the ions to recombine quite in check notwithstanding the strong electric attractions between them. But these electric forces introduce two sorts of viscous resistance which make the mobility of the ions a function of their concentration. This change of mobility is what the prevalent theory interprets as change of degree of ionization in strong electrolytes. In reality ionization is always complete in strong electrolytes at all concentrations. On these grounds it is plain why the current theory of physical chemistry fails to account for the variation of the conductivity of ordinary solutions with concentration, since the law of mass action is not in operation, being suppressed by the ionizing action of the solvent. The "dilution law" of Ostwald for the electric conductivity of aqueous solutions of acetic acid and similar weak electrolytes must have a different interpretation from that given to it in the text-books of physical chemistry, and seemingly accepted by a theoretical physicist like Planck (*Acht Vorlesungen über Theoretische Physik*, S. Hirzel, Leipzig, 1910). I have already suggested that in the case of such a weak electrolyte as acetic acid, the double molecules  $(\text{CH}_3\text{COOH})_2$  are partly dissociated in water into  $\text{CH}_3\text{COOH}$ , all of which is entirely ionized in accordance with the general principle stated above. On this view, the dilution law of Ostwald would express the equilibrium between the ions  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  acting as  $\text{CH}_3\text{COOH}$ , on the one hand, and  $(\text{CH}_3\text{COOH})_2$  on the other.

Here it may be objected, as by Walker at the Faraday Society's Discussion on the Constitution of Water (Trans. Faraday Soc. vi. 1910), that the molecular lowering of the freezing-point of water brought about by acetic acid shows that in dilute but only slightly ionized solutions of acetic acid the acid exists as  $\text{CH}_3\text{COOH}$  and not as  $(\text{CH}_3\text{COOH})_2$ . Here, again, I think we have to do with the application of an induction to a case which lies outside of its limits. It is easy to see that there are limits to the applicability of the lowering of freezing-point to the measurement of molecular mass. For instance, a little of a solvent added to itself does not lower the freezing-point. Consider next the case in which to a solvent

is added an isomeric form of itself having the same freezing-point. Here it is not to be expected that the rule of the molecular lowering of freezing-point will apply. The difference between the molecule of solute and of solvent must reach a limit of some sort before the rule applies. Similarly in another direction we must expect a limit to the applicability of the rule of molecular lowering of freezing-point. Imagine that in  $(\text{CH}_3\text{COOH})_2$  each of the  $\text{CH}_3\text{COOH}$  groups is so loosely attached to the other that they are just on the verge of parting company, then in relation to the molecules of solvent each  $\text{CH}_3\text{COOH}$  group has almost as much freedom of motion as if it were detached from the other. In such a case, until we have dynamical proof to the contrary, we may expect that the method of the lowering of the freezing-point will give the molecular mass as that of the nearly free  $\text{CH}_3\text{COOH}$  instead of its double. The difficulty seems to me analogous to that which arises in acidimetry when working with acid of strength comparable with that of the indicator. The lowering of freezing-point is generally a good indicator of molecular mass, but near the limits of its applicability, its results need careful collating with those from other sources. It seems to me that the theory of the physical chemistry of electrolytes has gone astray by accepting for a foundation the simplest chemical hypothesis which would account for Ostwald's dilution law for weak electrolytes, and also for the molecular lowering which they cause in the freezing-point of water. Originally, the primary object of the present paper was to test critically my suggestion as to the meaning of Ostwald's dilution law with weak electrolytes, but in the course of the work it seemed better to widen the scope of the inquiry, and to investigate a few typical solutions from the molecular dynamical point of view as far as seemed likely to be profitable in the absence of a kinetic theory of liquids. The solutions chosen are mixtures of ethyl alcohol and water to represent non-electrolytes, and mixtures of water with acetic and other fatty acids to represent weak electrolytes, all of which have been elaborately investigated by experimenters whose results have not received a correspondingly thorough study from the dynamical point of view, so that the theory of physical chemistry has been kept too narrow for the facts.

To these solutions the supporters of the hydrate theory of solutions have devoted some attention, tracing their salient peculiarities to the existence of hydrates, such as  $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$  in the case of alcohol, and  $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$  in that of acetic acid. It has been suggested that the

latter is even  $\text{CH}_3\text{C}(\text{OH})_3$ . Long ago Graham found that the mixture of acetic acid and water having the composition  $\text{CH}_3\text{COOH} + \text{H}_2\text{O}$  is the solution of maximum viscosity as well as of maximum density. Moreover,  $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$  has been isolated in the solid state like crystals with water of crystallization. But here again I shall try to show that there is excessive chemical simplification in the hypothesis that these hydrates exist as definite molecular structures in the solutions, and that a broader dynamical interpretation is to be given to the facts. The scheme of the following work is this :—

1. Formulation of the kinetic principle by which the properties of mixtures ought to be investigated.
2. Detailed examples of its application to the densities of solutions of ethyl alcohol and acetic acid in water and the contraction which occurs in their formation.
3. Similar results for all the other chief physical properties of mixtures of water with ethyl alcohol and with the first four of the series of fatty acids, namely molecular refraction and dielectric capacity, viscosity, specific heat and heat evolved on mixing, surface energy.
4. Conclusions to be drawn from these results.
5. Electric conductivity of solutions of the fatty acids.
6. Summary and general conclusions.

*1. Formulation of the Kinetic Principle by which the Properties of Mixtures ought to be investigated.*

For the particular case of potential energy this principle has been already stated in "Molecular and Electronic Potential Energy" (Phil. Mag. [6] xx. p. 249, 1910), and now it will be made generally applicable to all the properties of mixtures. The principle is fundamentally necessary in the theory of molecular potential energy advanced in many of my papers. Each molecule is simplified to an electrized sphere, similar to the Earth as a magnetized sphere, having a certain electric moment. The axes of electrization of contiguous molecules tend to adjust themselves in such a way that a molecule has its axis similarly directed to those of its two next axial neighbours, and oppositely directed to those of its four next lateral neighbours. In other words, the lines of electric force pass from an electrized molecule partly in almost straight lines to its two axial neighbours, and partly in closed curves through its four lateral neighbours, few lines wandering to any molecules beyond the six immediate

neighbours of a supposed cubical arrangement. If the arrangement were strictly and permanently cubical, then the axial lines of force would run on in continuous straight lines from molecule to molecule, as perhaps they do in crystals. But there would be no detectable free charge at a surface, because as many axial lines are directed in one way as in the opposite. In liquids it is better to imagine the axial lines at any instant not running far as nearly straight lines, but as closing their circuits by all sorts of interlaced paths. From this point of view it appears that if a few molecules of a liquid 1 are evenly distributed amongst many of liquid 2, the cohesive force between the molecules of liquid 1 cannot come into play, because the six immediate neighbours of a molecule of 1 are always molecules of 2. But experiments on the surface-tension of mixtures show that in this case the cohesive forces between the molecules of liquid 1 do come into operation. Hence we conclude that the molecules of liquid 1 are not evenly distributed, at any instant, amongst the molecules of 2, though they are evenly distributed on the average for a large number of instants. The most natural explanation of this fact is that the motion of the molecules causes a molecule of 1 to have another molecule of 1 for an immediate neighbour for a time which is a function of the properties of the two sorts of molecules. Thus we have a kinetic principle applying to all those properties of mixtures which depend on the relations of a molecule to its immediate neighbours, such as cohesion, density, viscosity, and the like. Let  $u_1$  be the amount of some property of unit mass of a pure liquid 1,  $u_2$  that of pure liquid 2, and let  $u_{12}$  be the amount for liquid 1 when a molecule of 1 is in contact with molecules of 2, and  $u_{21}$  the amount for liquid 2 when a molecule of 2 is in contact with molecules of 1. In general,  $u_{12}$  and  $u_{21}$  are functions of the concentrations, though they may become constants. Consider a mixture containing  $n_1$  molecules of 1 per unit volume and  $n_2$  of 2,  $n_{01}$  and  $n_{02}$  being the numbers for the pure substances. Then in the mixture a molecule of 1 may be assumed to be in contact with another of 1 as an immediate neighbour for the fraction  $n_1/n_{01}$  of its time: so being of mass  $m_1$  it carries the amount  $m_1 u_1 n_1/n_{01}$  of the property into the mixture, and the  $n_1$  molecules contribute  $m_1 u_1 n_1^2/n_{01}$ . Thus for the whole amount  $\rho u$  of the property in unit volume of the mixture we get

$$\rho u = m_1 u_1 n_1^2/n_{01} + n_1 n_2 (m_1 u_{12}/n_{02} + m_2 u_{21}/n_{01}) + m_2 u_2 n_2^2/n_{02}. \quad (1)$$

It is assumed that we have properly chosen the measure of the property so that its amount is obtained correctly by the additive process. This mixture formula (1) being of the second degree in  $n_1$  and  $n_2$  is markedly different from the usual empirical mixture formula linear in  $n_1$  and  $n_2$ . Let  $\rho$  denote density, and  $p$  mass of pure liquid per unit mass of mixture, then

$$n_{01}m_1 = \rho_1, \quad n_{02}m_2 = \rho_2, \quad n_1m_1 = p_1\rho, \quad \text{and} \quad n_2m_2 = p_2\rho,$$

$$\text{so} \quad \rho u = u_1 p_1^2 \rho^2 / \rho_1 + p_1 p_2 \rho^2 (u_{12} / \rho_2 + u_{21} / \rho_1) + u_2 p_2^2 \rho^2 / \rho_2. \quad (2)$$

To see how this formula of the second degree in  $p$  can reduce to the usual empirical formula of the first degree, let us suppose that

$$u_{12} / \rho_2 + u_{21} / \rho_1 = u_1 / \rho_2 + u_2 / \rho_1 \quad . \quad . \quad . \quad (3)$$

with  $u_{12} = u_1$  and  $u_{21} = u_2$  as the simplest case of all, then

$$\rho u = \rho^2 (p_1 u_1 + p_2 u_2) (p_1 / \rho_1 + p_2 / \rho_2) \quad . \quad . \quad . \quad (4)$$

If  $p_1 / \rho_1 + p_2 / \rho_2 = 1 / \rho$ , that is to say, if there is no contraction on mixing, the last formula takes the usual empirical form of the first degree in  $p$ , namely

$$u = p_1 u_1 + p_2 u_2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Our kinetic principle gives us, as it ought, the ordinary result when each molecule is supposed to carry all its properties unaltered into the mixture. Thus (1) and (2) are the equations that we need for investigating the changes occurring in the properties of molecules when they mingle with others of a different kind. A convenient way of using them is to write in general

$$u_{12} = u_1 + x_1, \quad u_{21} = u_2 + x_2, \quad p_1 / \rho_1 + p_2 / \rho_2 - 1 / \rho = \Delta,$$

thus fixing attention on the unknowns  $x_1$  and  $x_2$  which are the changes of  $u_1$  and  $u_2$  on mixing, and on  $\Delta$  which is the contraction per unit mass on mixing, we write (2) as

$$u = p_1 u_1 + p_2 u_2 + \rho \Delta (p_1 u_1 + p_2 u_2) + p_1 p_2 \rho (x_2 / \rho_2 + x_1 / \rho_1). \quad (6)$$

This equation separates the change of  $u$  from the value  $p_1 u_1 + p_2 u_2$  given by the linear mixture formula into two parts, that depending on the contraction, and that depending



on  $x_1$  and  $x_2$ . The latter term contains the factor  $p_1p_2$ , and as we shall see that  $\Delta$  depends chiefly on a factor  $p_1p_2$ , we have  $u - p_1u_1 - p_2u_2$  nearly containing a factor  $p_1p_2$ . This result reminds us that the law of mass action comes in with physical as well as with chemical change. If the closest packing of two sets of molecules is obtained when their numbers stand to one another in the ratio of two small integers, then we should have the two main conditions for chemical combination between them satisfied; we might, for instance, deduce the existence of hydrates, whose structure indicates the merging of chemical energies into physical, of intramolecular energies into intermolecular, rather than typical chemical combination. It is often forgotten that in a large part of the theory of solutions we are on a border where the separation between chemistry and physics becomes arbitrary, where we need to express ourselves in more general terms that will assume a mutual interdependence between intramolecular and intermolecular phenomena. Chemists have long been confronted with the same need in regard to water of crystallization. Molecular dynamics furnishes the appropriate means of expression.

## 2. *Detailed Examples of its Application to the Densities of Solutions of Ethyl Alcohol and Acetic Acid in Water and the Contraction which occurs in their Formation.*

Here we concentrate our study upon  $\Delta$  and put  $u=1/\rho$ , whereupon (6) becomes

$$\Delta + \rho\Delta^2/2 = -p_1p_2\rho(x_1/\rho_2 + x_2/\rho_1)/2 \quad . \quad . \quad (7)$$

and the immediate subject of investigation is

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = -(x_1/\rho_2 + x_2/\rho_1)/2 \quad . \quad . \quad (8)$$

Here  $x_1$  and  $x_2$  are not determined separately by means of the values of  $\Delta$  for each value of  $p_1$ . In the following table are given the data for ethyl alcohol and water, with the values of  $\Delta$  the contraction calculated from them and also those of  $(\Delta + \rho\Delta^2)/p_1p_2\rho$  on the left hand of (8) to serve for the study of  $-(x_1/\rho_2 + x_2/\rho_1)$  on the right.

TABLE I.

Contraction on making one gramme of mixture of Ethyl Alcohol and Water at 15° C. Alcohol as liquid 1, water as liquid 2,  $\rho_1=0.79356$ ,  $\rho_2=0.999216$ .  $100p_1$  is the percentage of alcohol by weight.

$100p_1$ .....	1	2	3	4	5	6	7
$10^5\rho$ .....	99725	99543	99367	99198	99034	98877	98726
$10^5\Delta$ .....	70	147	228	315	407	507	612
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	708	752	789	827	866	910	954
$100p_1$ .....	8	9	10	11	12	13	14
$10^5\rho$ .....	98581	98442	98307	98176	98050	97925	97803
$10^5\Delta$ .....	722	838	958	1082	1210	1339	1471
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	997	1044	1086	1131	1175	1216	1257
$100p_1$ .....	15	16	17	18	19	20	25
$10^5\rho$ .....	97683	97563	97443	97323	97202	97079	96429
$10^5\Delta$ .....	1604	1738	1871	2004	2135	2265	2865
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	1296	1328	1371	1407	1441	1473	1607
$100p_1$ .....	30	35	40	41	42	43	44
$10^5\rho$ .....	95686	94837	93891	93691	93488	93283	93076
$10^5\Delta$ .....	3357	3717	3951	3983	4012	4036	4055
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	1698	1753	1785	1791	1795	1798	1801
$100p_1$ .....	45	46	47	48	49	50	51
$10^5\rho$ .....	92866	92653	92438	92222	92005	91785	91564
$10^5\Delta$ .....	4072	4084	4093	4098	4102	4100	4087
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	1805	1807	1810	1814	1818	1821	1820
$100p_1$ .....	52	55	60	65	70	75	80
$10^5\rho$ .....	91341	90667	89526	88366	87189	85995	84778
$10^5\Delta$ .....	4090	4053	3944	3774	3543	3246	2874
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	1827	1840	1867	1908	1965	2041	2145
$100p_1$ .....	85	90	91	92	93	94	95
$10^5\rho$ .....	83531	82232	81964	81692	81417	81136	80852
$10^5\Delta$ .....	2409	1815	1677	1525	1375	1209	1036
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	2285	2473	2514	2549	2607	2651	2706
$100p_1$ .....	96	97	98	99			
$10^5\rho$ .....	80564	80269	79970	79665			
$10^5\Delta$ .....	853	656	449	230			
$10^4(\Delta+\rho\Delta^2/2)/p_1p_2\rho$ ...	2763	2813	2868	2917			

On account of their typical importance the data of this table have been given in great detail, especially near the decisive values of  $p_1$ , where the mixture is a dilute solution of alcohol in water, or of water in alcohol, or where  $p_1$  is nearly 0.5 and  $\Delta$  is close to its maximum. The densities are

derived from the German standard alcohol tables as given in the *Physikalisch-Chemische Tabellen* of Landolt and Börnstein, 3rd edition, from which source most of the subsequent data used in this communication will be derived. It will be noticed that  $10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  passes through a point of inflexion, which is actually, or almost, a minimax point near  $p_1=0.5$ . Its values show a certain symmetry in relation to that at  $p_1=0.5$ ; for, if this be subtracted from the values for  $p_1=0.9$  and  $0.1$ , the remainders are 652 and 735, for  $p_1=0.8$  and  $0.2$  the remainders are 324 and 348, and so on. At first this seemed to me to be a fact of perhaps fundamental significance, but we shall see that it is not so. After much study of the data in this table and related facts, I have been led to the following explanation of them. As alcohol is added to water it changes more and more of its trihydrol  $(\text{H}_2\text{O})_3$  into dihydrol  $(\text{H}_2\text{O})_2$ , the conversion being practically complete when  $p_1=0.5$ . If this is so, we can calculate the contraction  $\Delta$  for  $p_1=0.5$  by means of the data of "The Molecular Constitution of Water" (Phil. Mag. [5] l. p. 460, 1900). At  $15^\circ\text{C}$ . water is a mixture of 0.333 parts of  $(\text{H}_2\text{O})_3$  of density 0.88 with 0.667 parts of  $(\text{H}_2\text{O})_2$  of density 1.09, so that the contraction caused by changing 1 part of water into pure  $(\text{H}_2\text{O})_2$  is  $0.333(1/0.88 - 1/1.09) = 0.0728$ . If then  $\frac{1}{2}$  part of alcohol on mixing with  $\frac{1}{2}$  part of water changes it all into  $(\text{H}_2\text{O})_2$ , the contraction must be 0.0364, the corresponding tabulated number for the actual contraction being 0.0410. We shall look more closely into this soon. Consider now the case where the value of  $p_1$  is nearly 1, say 0.99, a little water being dissolved in a great excess of alcohol. We know that when water evaporates into the gaseous state it changes into hydrol  $\text{H}_2\text{O}$ . It is likely then that when a dilute solution of water is made in a solvent like alcohol, the water is changed for the most part into hydrol. Now in a contribution to the Faraday Society's Discussion on the Constitution of Water (Trans. Far. Soc. vi. 1910), I have shown that water of crystallization is hydrol having a density 1.26 in the liquid state at  $0^\circ\text{C}$ . If then 0.01 part of water on mixing with 0.99 part of alcohol is changed from density 1.0 to density 1.26, the contraction must be  $0.01(1 - 1/1.26) = 0.00206$  at  $0^\circ$ , the tabulated value being 0.00230 at  $15^\circ$ . Thus then we can give a fair account of the phenomena recorded in Table I. by the statement that as alcohol is added to water, it first converts its trihydrol into dihydrol, the change being nearly complete when the alcohol is nearly 50 per cent. of the mixture, and then when the alcohol is present in sufficient excess, it causes

the whole of the water to change into hydrol. Probably the two processes overlap a little. Nevertheless this explanation of the facts in Table I. implies that there is no significance in the symmetry pointed out above. From  $p_1=0$  to  $0.5$  the process is the change of trihydrol into dihydrol, from  $p_1=0.5$  to  $1$  it is the independent change of the dihydrol into hydrol. From the table we can now derive the laws of these changes. As Mendeléef froze out a mixture of alcohol and water having the composition  $C_2H_5OH + 3H_2O$ , which we shall see would be better written  $(C_2H_5OH)_2 + 3(H_2O)_2$ , it seems to me more prudent to assume that the potential energy conditions cause the whole of the change of trihydrol into dihydrol to be almost complete when a gram molecule of alcohol, that is 46 grams, is mixed with 3 gram molecules of  $H_2O$ , that is 54 grams. Thus we suppose the first process to end when  $p_1=0.46$ . The contraction due to the change of trihydrol into dihydrol in 0.54 parts of water is

$$0.54 \times 0.333(1/0.88 - 1/1.09) = 0.0393,$$

the tabulated value for  $p_1=0.46$  being 0.0408. The agreement between these two numbers is close enough to show the strong probability of the explanation now being proposed. It is reasonable to assume that the minimax in  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  near  $p_1=0.5$  is a maximum of the first process, that of converting trihydrol into dihydrol, at  $p_1=0.46$ , merging into the minimum at the commencement of the second process, that of changing the dihydrol into hydrol.

These considerations suggest the form

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = a + bp_1(0.92 - p_1) \quad \dots (9)$$

up to  $p_1=0.46$ , and with  $p_1(0.92 - p_1)$  as abscissa and the term on the left as ordinate a locus is obtained which is nearly a straight line with  $a=0.0655$  and  $b=0.5445$ , though the two halves of the locus have slight opposite curvatures. The maximum error of the contractions  $\Delta$  given by (9) is 3 per cent. As the maximum contraction is about 4 per cent. of the volume before mixing, it may be said that (9) gives the density of mixtures of alcohol and water up to  $p_1=0.46$  with a maximum error of the order of 1 part in 1000. We can take account of the curvatures just mentioned by using the more elaborate equations

from  $p_1(0.92 - p_1)=0$  to  $0.104$

$$\begin{aligned} (\Delta + \rho\Delta^2/2)/p_1p_2\rho = & 0.0655 + 0.5445p_1(0.92 - p_1) - 0.0027 \\ & + \{p_1(0.92 - p_1) - 0.052\}^2 \quad \dots (10) \end{aligned}$$

and from  $p_1(0.92 - p_1) = 0.104$  to  $0.2116$

$$= 0.0655 + 0.5445p_1(0.92 - p_1) + 0.0040 \\ - 1.5\{p_1(0.92 - p_1) - 0.155\}^2 \quad . \quad . \quad (11)$$

With these equations the density of mixtures of alcohol and water up to  $p_1 = 0.46$  is given with a maximum error of the order 2 in 10,000.

If the process we are studying is really the conversion of the trihydrol of water into dihydrol by alcohol up to  $p_1 = 0.46$ , then in interpreting  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  as  $-(x_1/\rho_2 + x_2/\rho_1)/2$  we shall have to give a somewhat complicated and arbitrary meaning to  $x_2$ , because, as the trihydrol is completely changed into dihydrol, the constituents of water when they come together in a mixture containing 46 per cent. of alcohol have never time to form water again, the effects of alcohol continue even when contact with alcohol has ceased. Either we must return to our original equation and treat  $\rho_2$  as a variable, or we must regard  $x_2$  as including changes caused remotely as well as immediately by contact with alcohol. It is simpler to interpret (9) in the following direct manner. Let water consist of  $a$  trihydrol and  $1-a$  dihydrol, and let  $\omega$  denote the contraction when a gram of trihydrol changes into dihydrol. Let  $p_1$  of alcohol convert the fraction  $f$  of the trihydrol  $ap_2$  in  $p_2$  of water, then the whole contraction on mixing is  $fap_2\omega = \Delta$ , which from (9), neglecting the small term  $\rho\Delta^2/2$ , is of the form

$$p_1p_2\rho\{b + cp_1(0.92 - p_1)\}.$$

For the moment treat 0.92 as 1, then this becomes

$$p_1p_2\rho(b + cp_1p_2),$$

that is to say,  $fap_2$  the mass of trihydrol changed into dihydrol by  $p_1$  alcohol consists of two parts, one proportional to  $p_1p_2$  due to the direct action of  $p_1$  alcohol on  $ap_2$  trihydrol, and the other proportional to  $p_1^2p_2^2$  and so due to a conjunction of two molecules of alcohol near two molecules of  $(\text{H}_2\text{O})_3$  in such a position as facilitates the change to  $3(\text{H}_2\text{O})_2$ . We may take the change from 1 to 0.92 to be due to a small term caused by the same conditions as make the potential energy a minimum when alcohol and water are in the proportion  $\text{C}_2\text{H}_5\text{OH}$  to  $3\text{H}_2\text{O}$ , that is 0.46 to 0.54 rather than 0.5 to 0.5.

So far we have neglected possible changes in the alcohol as cause of part of the contraction. The various empirical methods of determining the factor of association for alcohol at  $15^{\circ}$  C. give values of the order  $2 \pm 0.2$ . For the most part then alcohol consists of  $(C_2H_5OH)_2$ . Possibly some of this changes into  $C_2H_5OH$ . But my reasons for treating the amount of this change as negligible are first that the change of trihydrol into dihydrol accounts for the maximum contraction, that at the value of  $p_1$  for maximum contraction a hydrate separates out which must have the composition  $(C_2H_5OH)_2 + 3(H_2O)_2$  because only dihydrol is present. At this concentration of alcohol then there is probably no  $C_2H_5OH$  present; so it seems safe to assume that  $C_2H_5OH$  is not present at ordinary values of  $p_1$ . Perhaps in very dilute aqueous solutions of alcohol it may be found. But by the method of the lowering of the freezing-point it is currently held to have been ascertained that in all aqueous solutions of alcohol from  $p_1 = 0.0000185$  up to  $0.46$  the formula of alcohol is  $C_2H_5OH$ . If my previous arguments are sound, the contradiction here shown proves that the method of the lowering of the freezing-point breaks down for measuring the mass of the associated molecules of alcohol. It appears that in water the two  $C_2H_5OH$  groups are so loosely joined in  $(C_2H_5OH)_2$  that they lower the freezing-point as if they were free. Useful as the method may be in other ways, it is not adequate to decide whether the molecules of solutes in water are loosely associated or not. In connexion with acetic acid we shall see that the matter is important.

From  $p_1 = 0.46$  to  $1.0$  the law of the second process, the conversion of  $(H_2O)_2$  into  $H_2O$  is given by the equation

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.2979 - 0.59p_2(p_1^2 + 0.29p_2). \quad (12)$$

The coefficients in this equation are so related as not to give a real value of  $p_2$  for the minimum value of the left side, but they nearly allow a minimum close to  $p_2 = 0.57$  to join on to the maximum of (9) at  $p_1 = 1 - p_2 = 0.46$ . The equation gives the values of  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  with a maximum error of the order  $0.8$  per cent., and the densities with a maximum error of  $3$  in  $10,000$ . Its interpretation in a general way is that when  $p_1$  is greater than  $0.46$  the equilibrium between dihydrol and hydrol is determined by the occurrence of favourable conjunctions amongst the molecules. A broad approximate way of summarizing the information in Table I. is to take the mixture containing  $50$  per cent. of alcohol as a standard in which the water all

exists as dihydrol and  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.1821$ , and to write  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$

$$= 0.1821 - 0.414(0.25 - p_1p_2) \quad \text{for } p_1 < 0.5 \quad (13)$$

$$= 0.1821 + 0.375(0.25 - p_1p_2) \quad \text{for } p_2 > 0.5 \quad (14)$$

These equations probably tell us that in all cases the chief action between alcohol and water consists of two parts, one proportional to  $p_1p_2$  and the other to  $p_1^2p_2^2$ , which indicates that an important part is played by molecular conjunctions of two elements of alcohol and two elements of water. The net result is approximately that all the water is changed to dihydrol when  $p_1$  reaches 0.5 and to hydrol when  $p_1$  nearly reaches 1. Theoretically we must contemplate the coexistence of  $(\text{H}_2\text{O})_3$ ,  $(\text{H}_2\text{O})_2$ ,  $\text{H}_2\text{O}$ ,  $(\text{C}_2\text{H}_5\text{OH})_2$ , and  $\text{C}_2\text{H}_5\text{OH}$ . To keep the complications manageable for present purposes, I have neglected the amount of  $\text{C}_2\text{H}_5\text{OH}$  in all cases, the amount of  $\text{H}_2\text{O}$  when  $p_1 < 0.46$  or 0.5, and the amount of  $(\text{H}_2\text{O})_3$  when  $p_1 > 0.46$  or 0.5. If we calculate from  $\Delta$  when  $p_1$  is 0.46 the density of the trihydrol changed by alcohol into dihydrol of density 1.09, taking water at  $15^\circ \text{C}$ . to contain 1/3 of trihydrol, it comes out 0.873 at  $15^\circ$  in place of 0.88 at  $0^\circ$  deduced from the density of ice. So too, if we use (12) to find  $\Delta/p_2$  when  $p_2$  is small and find the density of hydrol with that of dihydrol 1.09, the result is 1.31 at  $15^\circ$  in place of 1.26 deduced from the densities of salts containing water of crystallization.

The case of acetic acid and water can now be presented briefly.

TABLE II.

Contraction on making 1 gramme of mixture of Acetic Acid and Water at  $15^\circ \text{C}$ . Acetic acid as liquid 1, water 2.  $\rho_1 = 1.0553$ ,  $\rho_2 = 0.9992$ .

$100p_1$ .....	1	2	3	4	5	6	8
$10^4\rho$ .....	10007	10022	10037	10052	10067	10083	10113
$10^5\Delta$ .....	100	190	290	390	480	580	770
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	1009	967	993	1010	1003	1020	1034
„ calc.	1003	1008	1012	1017	1021	1026	1035
$100p_1$ .....	10	20	30	40	50	60	70
$10^4\rho$ .....	10142	10284	10412	10523	10615	10685	10733
$10^5\Delta$ .....	948	1778	2441	2922	3214	3299	3185
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	1044	1090	1128	1175	1231	1309	1437
„ calc.	1044	1089	1134	1179	1224	1275	1428
$100p_1$ .....	80	90	92	94	96	98	
$10^4\rho$ .....	10748	10713	10696	10674	10644	10604	
$10^5\Delta$ .....	2784	1947	1700	1390	1020	570	
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	1638	2040	2173	2326	2496	2743	
„ calc.	1682	2038	2122	2209	2300	2396	

These data are represented by the equations

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.0999 + 0.045p_1$$

from  $p_1=0$  to  $0.5$  . . . (15)

$$= 0.1224 + 0.509(0.25 - p_1p_2)$$

from  $p_1=0.5$  to  $1$ , . . . (16)

the values of  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  given by these having been entered in the last line in Table II. Even in a 1 per cent. solution of acetic acid only about 1 per cent. of the acid is ionized, so that within the limits of Table II. we do not look for any appreciable effect of ionization on  $\Delta$ . Up to  $p_1=0.10$  the small irregularities in  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  are due to the want of sufficient refinement in the experimental data, the value of  $\Delta$  for  $p_1=0.01$  being obtainable correct only to 1 part in 10. But at the other extreme when  $p_1>0.9$  there is a progressively increasing discrepancy between the results of (16) and experiment, reaching 14 per cent. when  $p_1=0.98$ . To obtain the limiting value of  $\Delta/p_2$  when  $p_2$  is small, that is,  $p_1=1$  nearly, the following three equations have been found to summarize Table II. more accurately than (15) and (16) do, namely :

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.1000 + 0.044p_1$$

from  $p_1=0$  to  $0.5$  . . . (17)

$$= 0.1011 + 0.044p_1 + 0.3(0.25 - p_1p_2)$$

from  $p_1=0.5$  to  $0.77$  . . . (18)

$$= 0.1227 + 0.044p_1 + 2.39(p_1 - 0.77)^2$$

from  $p_1=0.77$  to  $1$ . . . (19)

When  $p_1=0.769$  the acetic acid and water are to one another as  $\text{CH}_3\text{COOH}$  to  $\text{H}_2\text{O}$ , the mixture being one of maximum density and maximum viscosity, though not of maximum contraction. It is probable that here the relations between acetic acid and water are such as give a relative minimum of potential energy helping to determine the chemical state of the water. I think that when  $p_1=0.77$ , for  $n$  molecules of  $(\text{CH}_3\text{COOH})_2$  there are  $n$  of hydrol and  $n/2$  of dihydrol, so that the mixture might be denoted by  $(\text{CH}_3\text{COOH})_2 + \text{H}_2\text{O} + \frac{1}{2}(\text{H}_2\text{O})_2$ , the reasons being that there is good evidence that at  $15^\circ\text{C}$ . acetic acid is  $(\text{CH}_3\text{COOH})_2$ , and that the contraction  $\Delta$  given by (18) and (19) for  $p_1=0.77$  is  $0.0294$ , while that deduced from the formula just



given is  $0.23 (1 - 1/1.09 + 1 - 1/1.26)/2 = 0.0332$ , which, in the circumstances, I take to be near enough to  $0.0294$  to justify provisionally the opinion that the maximum density and viscosity arise from the packing of the molecules of acetic acid and water as  $(\text{CH}_3\text{COOH})_2 + \text{H}_2\text{O} + \frac{1}{2}(\text{H}_2\text{O})_2$ . If this is so, then the chief difference of the action of acetic acid on water from that of alcohol on water is that from the very beginning acetic acid both destroys trihydrol and produces hydrol, whereas alcohol changes trihydrol to dihydrol first. So we should expect in both cases, when there is a large excess of alcohol or acetic acid, that the contraction will be that due to the conversion of all the water into hydrol. So the limiting value of  $\Delta/p_2$  for small values of  $p_2$  should be the same with alcohol and acetic acid and equal to  $1 - 1/1.26 = 0.2064$ . For alcohol from (12) this limiting value is  $0.2364$ , and for acetic acid from (19) it is  $0.3072$ . The discrepancy in the case of alcohol is not necessarily serious, as we are dealing with a limit, but in the case of acetic acid the difference between  $0.3072$  and  $0.2064$  is so large as to require scrutiny. The value  $0.3072$  would mean that in a large excess of acetic acid hydrol has a density  $1.443$  instead of  $1.26$ , which is the equivalent in the liquid state of  $1.31$ , the mean density of solid hydrol in crystals having water of crystallization. The largest density found for solid hydrol is that in  $\text{CuCl}_2 + 2\text{H}_2\text{O}$ , namely  $1.440$ , and the smallest is that in  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ , namely  $1.200$ . Thus we see that the discrepancy found in the case of acetic acid is only a little larger than that already observed with  $\text{CuCl}_2$  in relation to its water of crystallization. So it cannot be said that the discrepancy makes untenable the hypothesis that in excess of acetic acid water is changed into hydrol, but we must seek for further proof elsewhere, in connexion with other physical properties.

For mixtures of propionic and butyric acid with water densities at  $25^\circ\text{C}$ . are given by Lüdeking (*Wied. Ann.* xxvii. p. 72, 1886). These give for propionic acid and water with water as liquid 2 and  $\rho_1 = 0.9873$  :—

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.100 + 0.026p_1 \quad \text{from } p_1 = 0 \text{ to } 0.5 \quad (20)$$

$$\text{or} \quad = 0.107 \quad \text{from } p_1 = 0 \text{ to } 0.5 \quad (21)$$

$$\text{and} \quad = 0.113 + 0.38(0.25 - p_1p_2) \quad \text{from } p_1 = 0.5 \text{ to } 1. \quad (22)$$

These give  $\rho$  with a maximum error of the order 13 in

10000. For butyric acid and water the equations are with  $\rho_1=0.9521$ ,

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.089 \quad \text{from } p_1=0 \text{ to } 0.5. \quad . \quad . \quad (23)$$

$$= 0.089 + 0.5(0.25 - p_1p_2)$$

$$\text{from } p_1=0.5 \text{ to } 1. \quad . \quad . \quad (24)$$

These give  $\rho$  with a maximum error of 8 in 10000. For neither propionic acid nor butyric do the data extend beyond  $p_1=0.91$ , so that it is not possible to say whether (22) and (24) like (16) for acetic acid give a limiting value of  $\Delta/p_2$ , when  $p_2$  is small, which is rather less than the real limit. From (22) for propionic acid the limiting value of  $\Delta/p_2$  is 0.2053, and from (24) for butyric it is 0.2037, which are both close to 0.2064 for the change of all the water into hydrol of density 1.26. But equation (16) for acetic acid gives  $\Delta/p_2=0.2633$  in place of 0.3072 from the more accurate equation (19), so the values of  $\Delta/p_2$  just found from the data for propionic and butyric acids may be in error in a similar manner. It seems as though when acetic, propionic, and butyric acids are added to water in small amount, they first convert some of its trihydrol into dihydrol according to the simple formulas (15), (20), (21), and (23), and then when more acid is added, the conversion of dihydrol into hydrol becomes prominent, being completed when the mixture becomes a dilute solution of water in acid.

The case of formic acid and water requires some special attention on account of the known singularities of formic acid as the first of the fatty series. The densities in Table III. were found by Richardson and Allaire (*Amer. Chem. Journ.* xix. p. 149, 1897).

TABLE III.

Contraction on making 1 gramme of mixture of Formic Acid and Water at 20° C. 1 Formic acid as liquid 1, water 2,  $\rho_1=1.2213$ ,  $\rho_2=0.9983$ .

$100p_1$ .....	1	2	3	4	5	6	7
$10^4\rho$ .....	10020	10045	10071	10094	10116	10142	10171
$10^4\Delta$ .....	19	25	33	37	41	47	57
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	1910	1270	1130	950	850	820	86
$100p_1$ .....	8	9	10	20	30	40	50
$10^4\rho$ .....	10197	10222	10247	10489	10730	10964	1120
$10^4\Delta$ .....	64	69	75	117	148	164	180
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	850	820	813	703	661	627	649

Table III. (continued).

$100p_1$ .....	60	70	80	96	91	92	93
$10^4\rho$ .....	11425	11656	11861	12045	12060	12079	12100
$10^4\Delta$ .....	167	158	123	69	61	55	52
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	616	649	653	636	620	620	660
$100p_1$ .....	94	95	96	97	98	99	
$10^4\rho$ .....	12118	12141	12159	12171	12184	12203	
$10^4\Delta$ .....	46	43	37	27	18	11	
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$	670	740	790	760	750	910	

Here we see that as with alcohol the contraction is a maximum near  $p_1=0.5$ , though it is less than half the maximum contraction with alcohol. The most noteworthy fact is that  $10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  between  $p_1=0.3$  and  $0.94$  varies in an irregular manner between 700 and 600, so that we may write

$$(\Delta + \rho\Delta^2/2)/p_1p_2\rho = 0.0642 \quad \text{from } p_1=0.3 \text{ to } 0.93. \quad (25)$$

As  $p_1$  diminishes from 0.3 to 0.01 the value of  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  rises. Some densities given by Traube (*Ann. der Chem.* cclxv. 1891) for dilute formic acid solutions at  $15^\circ \text{C}$ . show a similar rise, but less, as shown in the following supplement to Table III.

$100p_1$ .....	0.574	1.148	2.288	4.547
$10^5\rho$ .....	100086	100237	100545	101174
$10^5\Delta$ .....	67	111	204	401
$10^4(\Delta + \rho\Delta^2/2)/p_1p_2\rho$ ...	117	98	91	92

This increase of  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  with diminishing small values of  $p_1$  did not appear with the other fatty acids or with alcohol. It cannot be ascribed to ionization, because, when  $p_1=0.1$ , only 1 per cent. of the formic acid is ionized, while  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  has gone up to 0.081 from 0.0642. With formic acid some special action takes place when  $p_1 < 0.3$ , perhaps the reduction of some higher polymer of  $\text{HCOOH}$  to  $(\text{HCOOH})_2$ . This requires special investigation. At the other limit when  $p_1 > 0.93$  the ratio  $(\Delta + \rho\Delta^2/2)/p_1p_2\rho$  rises, but its values are hardly consistent enough to let us estimate a limit for comparison with the limits for the other fatty acids and alcohol. If a little water in excess of formic acid is being changed partly into hydrol, the amount of change for a 1 per cent. solution of water in formic acid is only half of that for the other acids. A special experimental inquiry would be necessary to ascertain whether at

infinite dilution  $\Delta/p_2$  reaches the same or nearly the same limit with formic acid as with the next three acids of the fatty series. Probably the chief cause of the difference between the action of excess of formic acid on water and that of the other three acids is the fact that the dielectric capacity of formic acid is much nearer to that of water than is the case with the others. The dielectric capacities are about 80 for water, 60 for formic acid, 10 for acetic, 5 for propionic, and 3 for butyric. When a dilute solution of water is made with acetic, propionic, or butyric acid, the water is surrounded by substance of very different dielectric capacity from itself, and this difference seems to promote the splitting of dihydrol and trihydrol into hydrol. In formic acid the water is surrounded by a substance of more nearly its own dielectric capacity, and so dihydrol and trihydrol have more nearly the stability which they possess in water. In regard to ethyl alcohol similar considerations apply, as its dielectric capacity is 25. Of course dielectric capacity is only one of many factors controlling stability in such mixtures. By (25) for formic acid, if we neglect the small term  $\rho\Delta^2/2$ , we have  $\Delta$  proportional to  $p_1p_2\rho$ , which, except for the entrance of  $\rho$ , is the law deduced in "The Mol. Const. of Aqueous Solutions" (Phil. Mag. [6] xii. p. 1, 1906) for the contraction that occurs in the formation of aqueous electrolytic solutions. As solutions of formic and the other fatty acids at the dilutions we are studying are almost completely non-electrolytic, it is interesting to find a similar law for part of their contraction to that which holds for electrolytic solutions. It was shown in that paper that positive ions change trihydrol into dihydrol while negative ions change dihydrol into trihydrol. A gramme-equivalent of positive ion changes between 1.3 and 2.5 gramme-molecules of  $(\text{H}_2\text{O})_3$  into  $(\text{H}_2\text{O})_2$ , while a gramme-equivalent of negative ion forms out of  $(\text{H}_2\text{O})_2$  a number of gramme-molecules of  $(\text{H}_2\text{O})_3$  which ranges from 0.25 for  $\text{CO}_3$  to 1.57 for  $\text{CH}_3\text{COO}$  the acetic ion. From (15) for acetic acid, neglecting the small terms  $\rho\Delta^2/2$  and  $0.045p_1$ , it is easy, neglecting hydrol, to calculate the number of gramme-molecules of  $(\text{H}_2\text{O})_3$  converted into  $(\text{H}_2\text{O})_2$  by a gramme-molecule of  $(\text{CH}_3\text{COOH})_2$ , namely 1.014, say 1.0. Thus the action of  $(\text{CH}_3\text{COOH})_2$  in changing tri- into di-hydrol is nearly equal to that of a monovalent positive ion. We see clearly the importance of molecular and ionic electric fields in the causation of chemical change.

3. *Similar Results for all the other chief Physical Properties of Mixtures of Water with Ethyl Alcohol and with the first four of the series of Fatty Acids, namely Molecular Refraction and Dielectric Capacity, Viscosity, Specific Heat and Heat evolved on mixing, Surface Energy.*

As a rule molecular and atomic refraction are not convenient indicators of molecular change, for the chief generalization in relation to them is that each molecule and atom carries its molecular or atomic refraction unchanged through all physical and chemical changes. But there are notable exceptions to this rule, and in working out the molecular constitution of water the fact that  $(n^2 - 1)/(n^2 + 2)\rho$  for the D line at  $0^\circ \text{C}$ . has for trihydrol the value 0.20968, and for dihydrol 0.20434 proved helpful. Moreover, the average value for hydrol as water of crystallization is only about three-quarters of these. These facts suggest that the study of molecular refraction in the mixtures we are discussing should be expected to yield decisive results at once. But this expectation is disappointed in a very interesting manner. Let us first go back to the fundamentals of the subject. When Maxwell discovered his law  $K = n^2$ , he was confronted with remarkable exceptions in the commonest substances,  $K$  for water being of the order 80 and  $n^2$  of the order 2. The substances whose mixtures we are studying furnish marked exceptions to the law of Maxwell. I have suggested that in the case of water the large value of  $K$ , the ordinary dielectric capacity, is due to the pairs of electrons  $\sharp$  uniting the  $\text{H}_2\text{O}$  groups in  $(\text{H}_2\text{O})_3$  and  $(\text{H}_2\text{O})_2$ . The formula for tetravalent oxygen may be written  $\text{O}\mathfrak{b}_3\mathfrak{z}$ , in which  $\mathfrak{z}$  and  $\mathfrak{b}$  may form a doublet  $\sharp$  of small moment and cause O to become practically divalent  $\text{O}\mathfrak{b}_2$ . But on the other hand,  $\sharp$  may be opened out so that  $\mathfrak{z}$  joins with  $\mathfrak{b}$  from another opened out doublet, and the doublets become effective in building up  $(\text{H}_2\text{O})_3$  and  $(\text{H}_2\text{O})_2$ . When electric force acts upon these doublets, the effect is the same as that of magnetic force on magnetic material, and water has a large dielectric capacity for a reason similar to that which gives iron a large magnetic permeability. Why then does not this large dielectric capacity of water give it a correspondingly large index of refraction of the order 9 instead of the actual  $4/3$ ? The reason is that these valency electrons on account of their special chemical relation to the atom are constrained in such a way that they take but little part in the rapidly alternating movements of light. In the same way the other exceptions to Maxwell's law are to be ascribed to the

presence of doublets acting as chemical bonds. These doublets have an electric moment whose relation to the electric moment causing cohesion must be considered. In various papers on molecular attraction I have traced cohesion to the electrization of atoms, an atom being regarded as a sphere electrized in the same way as the earth is magnetized. It has an electric moment derived from the summation of the electric moments of the pairs of electrons  $\#$  out of which it is formed. According to the principle of minimum potential energy the axes of electrization of molecules adjust themselves so that the direction of the axis of a molecule is the same as that of its two axial neighbours and opposite to that of its four lateral neighbours. Each molecule attracts its six nearest neighbours, its alternate attraction and repulsion on remoter molecules being negligible in comparison with this concerted attraction on the six nearest neighbours. The attraction between two neighbour molecules is proportional to the product of their electric moments and inversely as the fourth power of the distance between their centres. It follows then that the electric moment of these doublets which act as special chemical bonds must modify cohesion. It is well known that associative liquids like water and ethyl alcohol are more cohesive than would be expected by analogy with the non-associative liquids, whence many of their exceptional properties. But in the case of water the cohesion is not increased nearly so much as we might be led to expect from the contrast between  $K$  of the order 80 and  $n^2$  of the order 2. The reason for this is again the fact that the special doublets acting as chemical bonds are subject to special constraint. The constitutive electron pairs in  $H_2O$  swing their axes round so that each molecule attracts its six nearest neighbours, but the three doublets in  $(H_2O)_3$  and the two in  $(H_2O)_2$  are not free to swing into position for attraction so quickly. They tend to do so where possible. Thus they increase cohesion, but not to the extent to be expected from the contrast between  $K$  and  $n^2$ . From these considerations it appears that the study of dielectric capacity in these mixtures is imperative if we are to understand the part played by atomic and molecular fields of electric force in determining the properties of our mixtures and the whole theory of solutions. For the normal dielectric capacity  $K$  which is equal to  $n^2$ , I have sought to show the dependence on electric moments in atoms ("The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity," *Phil. Mag.* [6] xix. p. 1, 1910). We shall now investigate as due to special electric moments in molecules those large

dielectric capacities which form the conspicuous exceptions to the law of Maxwell. Let  $e$  be the charge of  $\#$  and  $\flat$ , and let  $s$  be their distance apart in  $\#\flat$  which forms each of the three bonds in  $(\text{H}_2\text{O})_3$  or of the two in  $(\text{H}_2\text{O})_2$ . On the average the directions of the moments are uniformly distributed, so that we may replace each in imagination by one of electric moment  $es/2$  at right angles to any electric intensity  $X$  which is applied. The force on an electron is  $eX$ , which is equivalent to a tractive force  $eX/4a^2$  per unit area, if  $8a^3$  measures the share of space, or the domain, of  $\#\flat$ . If  $w$  is the rigidity of the molecule under this type of traction, each average pair of moment  $es/2$  has its axis sheared through an angle  $\theta = eX/4a^2w$ , so each electron at distance  $s/4$  from the centre of the pair is moved through a distance  $\theta s/4$  and the electric moment produced by  $X$  is  $e\theta s/4$  equivalent to an intensity of electrization  $e\theta s/32a^3$ , which is often written  $kX$  with the relation  $4\pi k + 1 = K$ . Hence

$$K - 1 = 4\pi k = \pi e^2 s / 32 a^3 w. \quad . \quad . \quad . \quad (26)$$

I shall apply this equation first to the case of ice with the simplifying assumption that  $w$  is equal to the rigidity of ice at its melting-point. In "The Molecular Constitution of Water" it has been shown that the melting of ice is not an ordinary melting at all, it is the sudden breaking down of  $(\text{H}_2\text{O})_3$  into a solution of  $(\text{H}_2\text{O})_3$  in  $(\text{H}_2\text{O})_2$ . It is reasonable to assume then that the rigidity of ice at  $0^\circ \text{C}$ . is partly the rigidity of each  $(\text{H}_2\text{O})_3$  due to the bonds  $\#\flat$ , and may be roughly taken for  $w$ . The Young's modulus of ice was found by Reusch acoustically to be 23632 kg. weight/cm.<sup>2</sup>, and by Hess (*Ann. d. Phys.* viii. p. 405, 1902) on the average  $2.54 \times 10^{10}$  c.g.s. So we assume  $3w = 2.5 \times 10^{10}$ . If we take  $8a^3$  as the sum of the values of  $\text{H}_2$  and  $\text{O}$ , namely  $10^{-24}$  ( $2 \cdot 17^3 + 2 \cdot 71^3/2$ ) and  $e = 4.65 \times 10^{-10}$  with  $K - 1 = 80$ , we get  $s/2a = 0.5$ , that is to say, that our simplifying assumptions make  $s$  of the order of magnitude of  $2a$  the diameter of  $\text{H}_2\text{O}$ . This result shows that our general principle of accounting for the large  $K$  of ice and water by the electric moment  $es$  is probably sound. We expect  $s$  to be actually only a fraction of  $2a$ , a result which we should have obtained if we had assumed  $w$  to be only a fraction of the rigidity of ice, which is more likely to be true than our assumption that  $w$  is equal to the rigidity of ice. As  $K$  is nearly the same in water and in ice, we obtain the interesting result that on account of the bonds  $\#\flat$  in  $(\text{H}_2\text{O})_3$  and  $(\text{H}_2\text{O})_2$  each molecule of water has a rigidity of its own.

We can carry the inquiry a step farther by treating the

rigidity  $w$  as due to the same electric doublets  $\#p$  as cause  $K-1$ . By "The Electric Origin of Rigidity, &c." (Phil. Mag. [6] xvii. p. 417)  $w = (2\pi/3K)(e^2s^2/2^6a^6)$ , in which  $K$  may be put equal to 1. In this case then

$$K-1 = 3a/s, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and  $s/2a$  is only about 0.02. Thus, if the rigidity resisting displacement of the average doublet has its origin in that doublet,  $K-1$  varies inversely as  $s$ , that is, inversely as the electric moment of the doublet, whereas if the rigidity is of independent origin, we saw by (26) that  $K-1$  is directly proportional to  $s$ . In intermediate cases we have an intermediate relation between these two. These principles then along with those established in "The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity" give a theory of dielectric capacity in general, whether conforming to Maxwell's law or exceptional.

Concerning large exceptional dielectric capacities, great importance seems to me to belong to Abegg's discovery of the law of their variation with temperature, a law to be ranked with the corresponding discovery of J. Curie concerning paramagnetism. The law of Abegg (Wied. Ann. lx., lxx., *Ztschr. f. ph. Ch.* xxix.) is that the five alcohols from methyl to amyl, nitrobenzol and water have the same value of  $-dK/KdT$  from ordinary temperatures  $T$  down to the point of solidification, namely  $1/190$ . Probably a better statement would be that  $-d(K-1)/(K-1)dT$  is constant and the same for these different substances down to temperatures near those of solidification. This law makes it appear that the large exceptional value of  $K-1$  has a similar origin in these different substances, and this origin I take to be the pair of electrons  $\#p$  effective in causing association of their molecules. If we neglect the small variations of  $a$  with temperature, we get from (27) that  $-d(K-1)/(K-1)dT = ds/sdT$ , which by the law of Abegg must be the same for these different substances. If we regard  $dT$  as measuring increment of kinetic energy of the oxygen atoms bound by  $\#p$ , then the law of Abegg means that the increase of the electric moment  $es$  of  $\#p$  due to  $dt$  is proportional to  $s$  and to  $dT$ . This gives a clue to the connexion between the potential energy of the doublets  $\#p$  and kinetic energy in the molecule. In applying these considerations to our mixtures we shall begin with

#### *Molecular Refraction.*

Both  $(n-1)M/\rho$  and  $(n^2-1)M/(n^2+2)\rho$  may be used as the measure of this. For present purposes too we may



drop out  $M$  and denote  $(n-1)/\rho$  by  $r$  and  $(n^2-1)/(n^2+2)\rho$  by  $r'$ . In (6) we put  $u=r$  or  $r'$  and get

$$r=p_1r_1+p_2r_2+(p_1r_1+p_2r_2)\rho\Delta+p_1p_2\rho(x_1/\rho_2+x_2/\rho_1). \quad (28)$$

In the simplest kind of mixture  $\Delta=0$  and  $r=p_1r_1+p_2r_2$ , so that  $x_1/\rho_2+x_2/\rho_1=0$ , probably because  $x_1=0=x_2$ . But when  $\Delta$  does not vanish, as in the mixtures we are studying, then we see that an important part of  $r-p_1r_1-p_2r_2$  is directly proportional to the contraction  $\rho\Delta$  on forming unit volume of the mixture. If we denote  $p_1r_1+p_2r_2$  by  $r_c$  to indicate that it is a value of  $r$  calculated by the simple rule of mixtures, we can write (28) thus :

$$\frac{r-r_c}{r}=\rho\Delta+p_1p_2\rho(x_1/\rho_2+x_2/\rho_1)/r_c. \quad (29)$$

Pulfrich has shown that in such cases  $(r-r_c)/r_c$  is proportional to  $\rho\Delta$ , and Hess has devoted a paper chiefly to the investigation of Pulfrich's formula with mixtures of water with alcohol and acetic acid (*Ann. der Phys.* xxvii. p. 589, 1908). He finds that on the average with alcohol  $(r-r_c)/r_c=0.977\rho\Delta$ , the coefficient ranging from 0.929 when  $p_1=0.2$  to 1.04 when  $p_1=0.8$ . In (29) for alcohol we may say that  $x_1/\rho_2+x_2/\rho_1=0$ . With acetic acid according to the investigation of Buchkremer, quoted by Hess, the mean numerical coefficient is 1.11, ranging from 1.04 when  $p_1=0.14$  to 1.14 when  $p_1=0.7$ . With acetic acid too  $x_1/\rho_2+x_2/\rho_1$  is nearly 0. With  $r'$  the results are similar, the numerical coefficient for alcohol being 0.8852, and for acetic acid 1.0033. Having found in this survey of the broad facts that the term in  $p_1p_2\rho$  in (29) cannot at present be detected in a useful manner, we can investigate molecular refraction in a different way if we use the ideas gained in studying contraction. The chief idea is that all the change takes place in the water, none in alcohol or acetic acid. If then we assume that  $r$  or  $r'$  is unchanged for liquid 1, we can calculate from the data for any mixture the value for  $r_2$  or  $r'_2$  for water as the changed liquid 2. I shall use  $r'$ , having already used it in investigating the molecular constitution of water. In

$$\left. \begin{aligned} r' &= p_1r'_1 + p_2r'_2 \\ \text{that is } (n^2-1)/(n^2+2)\rho &= p_1(n_1^2-1)/(n_1^2+2)\rho_1 \\ &\quad + p_2(n_2^2-1)/(n_2^2+2)\rho_2 \end{aligned} \right\} \quad (30)$$

we know  $r'_1$ , and also  $r'$  for each value of  $p_1$ , or  $n_1$  and  $n$

for each value of  $p_1$ , so we can calculate  $r_2'$ , that is  $(n_2^2 - 1)/(n_2^2 + 2)\rho_2$  for the changing liquid 2, water, the change in the constitution of the water showing itself by small changes in the value of  $r_2'$ . For alcohol and water the data are those of Hess at 15° C. for the line F of the spectrum. From the density 0.80889 at 15° C. of Hess's alcohol it appears that it was a 95 per cent. spirit by weight. This fact will not interfere with our method of inquiry, which is the main thing at the present stage. With alcohol (95 per cent.) as liquid 1 and water as liquid 2 the results are :

$10^5 p_1$ .....	0	20751	40890	59993	79865
$10^5 r_2'$ .....	20854	20783	20738	20751	20879

If these data are represented on a graph they show a minimum of  $r_2'$  near  $p_1 = 0.5$ , perhaps at 0.46, having a value 0.20733. Since at 15° C. water is two-thirds  $(\text{H}_2\text{O})_2$  and one-third  $(\text{H}_2\text{O})_3$ , and at 0° C.  $r' = 0.20968$  for the D line of the spectrum with  $(\text{H}_2\text{O})_3$  and 0.20434 for  $(\text{H}_2\text{O})_2$ , we find by proportion that at 15° C. with the F line  $r' = 0.21214$  for  $(\text{H}_2\text{O})_3$  and 0.20674 for  $(\text{H}_2\text{O})_2$ . Thus the decrease in  $r_2'$  with increasing  $p_1$  from  $p_1 = 0$  to 0.5 means that as the alcohol is increased it converts more and more trihydrol into dihydrol, as we found to be the case in studying contraction. If the conversion were complete and uncomplicated by any other change when  $p_1 = 0.46$  and the mixture is  $(\text{C}_2\text{H}_5\text{OH})_2$  with  $3(\text{H}_2\text{O})_2$ , then the minimum found for  $r_2'$  ought to be 0.20674 for  $(\text{H}_2\text{O})_2$  instead of 0.20733 as estimated from the graph of the above data. On the whole refraction confirms the conclusion from contraction, that up to  $p_1 = 0.5$  or 0.46 the chief action of alcohol on water is to change all its trihydrol into dihydrol. The refraction data would make it appear that the change is never complete, but the increase of  $r_2'$  when  $p_1 > 0.5$  shows another action taking place, and perhaps part of this action occurs before  $p_1 = 0.5$  and so masks part of the change in  $r_2'$  due to change of  $(\text{H}_2\text{O})_3$  into  $(\text{H}_2\text{O})_2$ . This other action we identified in the study of contraction as the change of dihydrol into hydrol. If this is correct, it appears that  $r'$  for hydrol is greater than for dihydrol. This raises a temporary difficulty, because in my contribution to the Faraday Society discussion I found that hydrol in the form of water of crystallization has a much smaller  $r'$  than dihydrol or trihydrol. The last little table makes it plain that here we have to do with hydrol possessing a larger  $r'$  than dihydrol. A graph of the data shows that for an infinitely dilute solution of water in alcohol  $r_2'$  has a limiting value like 0.2107 or 0.2110.

Lorenz's value for the D line for vapour of water, hydrol, is 0.2068 equivalent to 0.2092 for the F line. Refraction then confirms the result obtained from contraction that the action of alcohol on water may be divided into two processes: first the conversion of trihydrol into dihydrol, and second the conversion of dihydrol into hydrol, whose optical properties are nearly those of vapour and not of water of crystallization, but refraction makes it appear that the two processes overlap. For the complete investigation of these interesting problems we require at definite temperatures the most accurate obtainable measurements of density and index of refraction for mixtures of absolute alcohol and water. Let the water in any mixture contain in 1 gramme  $x_3$  gramme of hydrol,  $x_4$  of dihydrol, and  $x_5$  of trihydrol, then we have the equations

$$\left. \begin{aligned} 1 &= x_3 + x_4 + x_5 \\ 1/\rho &= p_1/\rho_1 + p_2(x_3/\rho_3 + x_4/\rho_4 + x_5/\rho_5) \\ r &= p_1r_1 + p_2(x_3r_3 + x_4r_4 + x_5r_5) \\ 1 &= p_1 + p_2 \end{aligned} \right\} \quad . \quad (31)$$

By special experiments carried towards an infinitely dilute solution of water in alcohol  $x_4$  and  $x_5$  may be made negligible so that  $\rho_3$  and  $r_3$  may be found, and then the equations give from the experimental data the values of  $x_3$ ,  $x_4$ , and  $x_5$  for each value of  $p_1$  at each temperature. In some such way, no doubt, the whole of the phenomena will be investigated, so I shall not try to push farther at present with the published data for alcohol and water.

Treated in the same way the data of Buchkremer for acetic acid and water at 20° C. with the D line of the spectrum yield the table

$10^5 p_1 \dots\dots$	0	15077	32125	45686	61948	72223	84504
$10^5 r_2' \dots$	20612.5	20605	29606	20648	20664	20704	20717

For acetic acid  $r_1' = 0.21675$ . Here as with alcohol we have first a decrease of  $r_2'$  with increase of  $p_1$ , a graph showing a minimum of value 0.20597 about  $p_1 = 0.25$  and a maximum estimated as 0.2077 for an infinitely dilute solution of water in acetic acid. To compare this limit for the D line with 0.2107 or 0.2110 obtained from alcohol with the F line, we notice that for water the difference in  $r'$  for D and F is  $0.206125 - 0.20854 = -0.002415$ , so that 0.2077 for the D line with acetic acid means 0.2101 for the

F line, which is near to the two alternative values for water dissolved in an infinite volume of alcohol. This tends to confirm our conclusion from contraction that water in an infinite volume of acetic acid is changed into hydrol. Returning to the minimum, we see that it is caused by the conversion of trihydrol into dihydrol which lowers  $r_2'$  until the process of changing dihydrol into hydrol with larger  $r_2'$  brings the diminution to an end and gives the minimum. In the study of contraction we concluded that with acetic acid the process of forming hydrol makes itself apparent at much smaller values of  $p_1$  than in the case of alcohol. Refraction confirms this result. I shall not analyse existing experimental facts in greater detail as I think we need, as with alcohol, a special set of experiments for  $\rho$  and  $r'$  at different temperatures, the data to be handled by means of equations (31).

#### *Dielectric Capacity.*

Here the experimental and theoretical difficulties are well known in connexion with mixtures. I shall make  $(K-1)/\rho$  the subject of study with the supposition that for an ideally simple mixture

$$(K-1)/\rho = p_1(K_1-1)/\rho_1 + p_2(K_2-1)/\rho_2 \quad . \quad . \quad (32)$$

In our exceptional mixtures we shall regard  $(K_2-1)/\rho_2$  as varying with  $p_1$  on account of the changes occurring in water as liquid 2, and shall calculate values of  $(K_2-1)/\rho_2$  from those of  $(K-1)/\rho$  by (32). For alcohol and water we have the data of Nernst (*Tabellen*) from 19° C. to 20°, say 20°, and those of Thwing (*Ztschr. f. ph. Chem.* xiv. p. 286, 1894) at 15° C. Thwing's results for mixtures of associating liquids and for water showed some remarkable singularities, which in the case of mixtures he interpreted as due to hydrates or similar compounds. In the case of water he found a sharp maximum for  $K$  at 4° C. This maximum was specially looked for by Vonwiller (*Phil. Mag.* [6] vii. p. 655, 1904) but not found, nor have Thwing's singularities for mixtures been found by other experimenters. Yet Thwing's values for pure substances and for water not near 4° C. agree well with other determinations and the general course of his values for mixtures of associating liquids agrees with that of other observers. Nernst's data give the results:—

100 $p_1$ .....	100	90	80	70	60	50
$K$ .....	26	29.3	33.5	38.0	43.1	48.5 (about)
$(K_2-1)/\rho_2$ .....	...	61.0	65.5	68.7	70.2	72.0

From the measurements of Drude and Heerwagen we know that at  $20^{\circ}$  C.,  $K$  for water is 80, so that in the limit with pure water  $(K_2-1)/\rho_2$  is 79. So it appears that 50 per cent. of alcohol in a mixture reduces  $(K_2-1)/\rho_2$  from 79 to 72, while 90 per cent. of alcohol reduces it to 61. Since  $(K-1)/\rho$  for ice and for water at  $0^{\circ}$  C. are nearly equal, they are nearly equal for trihydrol and dihydrol. Hence as the change caused by alcohol as it is increased from 0 to 50 per cent. is chiefly that of trihydrol into dihydrol, the value 72 for  $(K_2-1)/\rho_2$  when  $p_1=0.5$  is but little different from 79, a result confirming our general conclusion as to the first process when alcohol is mixed with water. As  $p_1$  is increased from 0.5, the second process of changing dihydrol into hydrol goes on. It appears that  $(K-1)/\rho$  for hydrol must be less than for dihydrol, since  $(K_2-1)/\rho_2$  in the above table diminishes with increase in the amount of hydrol.

Thwing's values at  $15^{\circ}$  C. are :—

100 $p_1$ .....	100	90	80	70	60	50	40	30	20	10
$K$ .....	25.02	25.71	28.15	33.66	36.31	44.11	48.40	59.55	61.79	67.95
$(K_2-1)/\rho_2$ .	...	28	39	54.7	53.2	63.8	64.0	74.3	70.7	74.5

Thwing found  $K$  for water to be 75.5 at  $15^{\circ}$  C., so that with his data the limiting value of  $(K_2-1)/\rho_2$  for pure water is 74.5. Mixtures containing 10 per cent. of alcohol and 30 per cent. give practically the same result with a fall to about 64 when  $p_1=0.5$ . The conclusion to be drawn agrees with that from Nernst's datum for  $p_1=0.5$ . For larger values of  $p_1$  the value of  $(K_2-1)/\rho_2$  diminishes as it did before, but in a more pronounced manner. The chief differences between Nernst's and Thwing's results might be explained on the supposition that under the conditions of the experiments hydrol had a much smaller  $K$  in Thwing's than in Nernst's. In Nernst's experiments with 79 for the limit of  $(K_2-1)/\rho_2$  for pure water  $79-(K_2-1)/\rho_2$  is nearly proportional to  $\Delta/p_2$  the corresponding contraction of unit mass of water, obtainable from Table I., thus :—

100 $p_1$ .....	90	80	70	60	50
$79-(K_2-1)/\rho_2$ ...	18	13.5	10.3	8.8	7
$10^4 \Delta/p_2$ .....	1815	1437	1181	986	820

We have nearly

$$79-(K_2-1)/\rho_2=92\Delta/p_2,$$

and more roughly for Thwing's results

$$74.5-(K_2-1)/\rho_2=214\Delta/p_2.$$

If we regard the water in 50 per cent. alcohol as dihydrol which is changed by more alcohol into hydrol, and if we take  $\Delta/p_2 = 0.082$  to measure the amount of this change, the relation for Nernst's data becomes

$$(K_2 - 1)/\rho_2 - 72 = 106(\Delta/p_2 - 0.082),$$

and for Thwing's

$$(K_2 - 1)/\rho_2 - 63.8 = 375 (\Delta/p_2 - 0.082).$$

An observation of Abegg's is of great interest. He found his law hold for a mixture of 10 volumes of ethyl alcohol with 1 volume of water down to  $-83^\circ.6$  C., K for the mixture being given by  $145e^{-T/190}$ . He found, moreover, that if he applied the simple mixture formula (32) to his results, he got for water in alcohol below  $0^\circ$  C.

$$K = 372e^{-T/190},$$

a formula which applies excellently to the experiments of Heerwagen and Drude on water up to  $76^\circ$  C. It is very remarkable that, though water is a mixture whose composition varies with temperature, it should have K given by this simple formula, which confirms the conclusion that K for trihydrol is nearly equal to K for dihydrol and is produced by the same mechanism in both substances, the  $\#b$  bond joining O to O in  $(H_2O)_3$  and  $(H_2O)_2$ . In the same way Abegg's discovery that K for a mixture of alcohol and water conforms to his law, shows that in alcohol and water the same mechanism confers the large abnormal K. But Abegg's result for the mixture brings in a seeming difficulty. In his mixture  $p_1 = 0.89$ . But we have seen that in Nernst's experiments 90 per cent. of alcohol changes  $(K_2 - 1)/\rho_2$  for water considerably, and in Thwing's much more, whereas in Abegg's 89 per cent. alcohol causes no change. It appears then that liquid hydrol has a K which varies much with the experimental conditions, being equal to that of K for water under those of Abegg, but much smaller under those of Thwing. Now at the Faraday Society's discussion I brought out the fact that in water of crystallization hydrol has a value of K about 6. As water of crystallization is hydrol in the solid state, this recalls Abegg's observation that when the alcohols solidify, the large value of K for the liquid changes to a value nearly equal to  $n^2$  in accord with the law of Maxwell. It appears then that the whole of this subject is full of interesting clues to the functions of electrons in

molecular architecture. With Thwing's experiments on acetic acid and water the results are :—

100 $p_1$ .....	30	40	50	60	62.5	70	74	77	80
$(K_2-1)/\rho_2$ ...	83	90	104	127	135	99	102	116	67

For water  $(K_2-1)/\rho_2$  is 74.5. It appears then as though in these experiments, except when  $p_1=0.8$ ,  $(K_2-1)/\rho_2$  for hydrol is larger than for dihydrol.

### *Viscosity and Fluidity.*

For the adequate treatment of this subject a dynamical theory of the viscosity of liquids is most desirable. Though Jaeger and Brillouin among others have prepared the way for such, deductive methods have not yet led to a rational formula connecting the viscosity of a mixture with that of its ingredients. On the experimental and empirical side it has been found that a formula

$$\eta = p_1\eta_1 + p_2\eta_2$$

for the viscosity of a mixture is often too rough an approximation to the truth. Sometimes

$$\eta/\rho = p_1\eta_1/\rho_1 + p_2\eta_2/\rho_2$$

performs better, in other cases worse. Bingham has found that  $1/\eta$ , the fluidity, can be fairly well represented by the simple mixture formula

$$1/\eta = p_1/\eta_1 + p_2/\eta_2 \quad . \quad . \quad . \quad . \quad . \quad (33)$$

and leads to general relations between viscosity and chemical structure (Amer. Chem. Journ. xxxv. p. 195, 1905; *Ztschr. f. ph. Chem.* lxvi. p. 1 & p. 238, 1909). So with our abnormal mixtures I shall investigate viscosity  $\eta$  through its reciprocal  $1/\eta$  the fluidity. Though the viscosity of liquids is not far advanced on the theoretical side, its experimental contributions to our subject are most helpful. Ever since Graham found a maximum viscosity in mixtures of water and alcohol corresponding with its maximum density, and a similar result was established for mixtures of water and acetic acid, many experiments have been devoted to the phenomenon, because it brings out so emphatically the occurrence of rather profound molecular re-arrangements. For instance, at 25° C. the viscosity of water is 0.00891, of alcohol 0.01113, while the maximum viscosity, when  $p_1=0.46$ , is 0.02368.

In "The Mol. Const. of Water" I have shown that the viscosity of water is chiefly due to its trihydrol, having estimated that at 0° C.  $\eta$  for trihydrol is 0.0381 and for

dihydrol only 0.0030. This is rather an unexpected result that the less dense form of a substance should have the larger viscosity, but it is due to the fact that the normal physical melting-point of trihydrol, if ascertainable, would be found to be above the melting-point of ice, and that of dihydrol to be below it. This being so, it might seem that the effect of adding alcohol to water, if it changes trihydrol into dihydrol, would be to lower the viscosity below, or raise the fluidity above, that given by the simple mixture formula, to give a minimum of viscosity and not a maximum. Here then we encounter another difficulty which may prove instructive. We must remember that viscosity in a liquid is determined largely by the conditions ruling in the inter-space between neighbour molecules. Thus alcohol, though it changes trihydrol into the less viscous dihydrol, may at the same time have its molecules brought nearer to the other molecules of the mixture in such a way as to increase the viscosity due to their mutual relations. If this increase exceeds the decrease due to change of trihydrol, the viscosity may rise to a maximum. Here then is a case where (6) is useful, because in  $x_1$  and  $x_2$  it provides measures of the changes brought about by the changed relations of molecules of 1 and 2 as neighbours. In that equation we put  $u=1/\eta$  and study

$$\{1/\eta - p_1/\eta_1 - p_2/\eta_2 - (p_1/\eta_1 + p_2/\eta_2)\rho \Delta\} / p_1 p_2 \rho = x_1/\rho_2 + x_2/\rho_1. \quad (34)$$

The data in the next table for ethyl alcohol and water are those of Dunstan (*Journ. Chem. Soc.* lxxxv. p. 817, 1904), from which the left-hand member of (34) is calculated to enable us to study the right-hand.

TABLE IV.

## Viscosity of Ethyl Alcohol and Water at 25° C.

100 $p_1$ .....	0.0	3.6	5.09	12.50	16.00	24.66	29.63
10 <sup>5</sup> $\eta$ .....	891	959.6	1013	1356	1552	1851	2129
$-x_1/\rho_2 - x_2/\rho_1$ ...	...	215	268	346	350	311	312
100 $p_1$ .....	32.40	37.39	38.26	41.21	46.17	47.72	50.20
10 <sup>5</sup> $\eta$ .....	2162	2290	2301	2527	2368	2354	2337
$-x_1/\rho_2 - x_2/\rho_1$ ...	286	291	289	283	278	275	272
100 $p_1$ .....	55.58	55.83	57.51	60.15	60.17	60.49	61.06
10 <sup>5</sup> $\eta$ .....	2273	2273	2247	2243	2240	2226	2212
$-x_1/\rho_2 - x_2/\rho_1$ ...	268	268	267	271	270	270	269
100 $p_1$ .....	65.36	65.85	70.54	73.90	80.20	100	
10 <sup>5</sup> $\eta$ .....	2104	2112	1995	1957	1744	1113	
$-x_1/\rho_2 - x_2/\rho_1$ ...	268	271	275	287	294		



The requisite values of  $\Delta$  and  $\rho$  for use in (34) have been obtained from Table I. by interpolation,  $(p_1/\eta_1 + p_2/\eta_2)\rho\Delta$  being at the most only 6 per cent. of  $1/\eta - p_1/\eta_1 - p_2/\eta_2$ . The table shows that  $x_1/\rho_2 + x_2/\rho_1$  is nearly constant throughout, though it starts with a small value and rises to a maximum when  $p_1 = 0.16$ , increasing again at the largest  $p_1$ . The main fact then is that  $x_1/\rho_2 + x_2/\rho_1$ , during the change of trihydrol into dihydrol, is not much different from its value during the change of dihydrol into hydrol. Thus, while the course of viscosity emphasises the total change, it does not differentiate sharply the two chief processes of which the change consists.

The data used for viscosity of the fatty acids in the next table are those of Tsakalotos (*Comptes Rendus*, cxlvi. p. 1146, 1908).

TABLE V.

At 20°, Viscosity of Water and

Formic Acid.

100 $p_1$ .....	0	20.2	40.6	61.1	68.4	74.5	77.2	87.1	100
$10^3 \rho$ .....	998.2	1049	1098	1143	1159	1171	1176	1192	1216
$10^3 \eta$ .....	1003	1108	1246	1430	1480	1535	1576	1669	1780
$-x_1/\rho_2 - x_2/\rho_1$ ..	...	10	13	17	15	15	18	19	

Acetic Acid.

100 $p_1$ .....	0	22.3	40.7	50.4	62.2	71.2	77.9	85.6	100
$10^3 \rho$ .....	998.2	1026	1046	1055	1064	1068	1069	1067	1052
$10^3 \eta$ .....	1002	1502	1930	2188	2404	2617	2716	2344	1286
$-x_1/\rho_2 - x_2/\rho_1$ ..	...	169	165	174	190	222	262	306	

Propionic Acid.

100 $p_1$ .....	0	34.6	68.9	74.2	79.8	90	100		
$10^3 \rho$ .....	998.2	1022	1025	1023	1020	1012	994.5		
$10^3 \eta$ .....	1003	1982	2752	2794	2973	2622	1114		
$-x_1/\rho_2 - x_2/\rho_1$ ..	...	209	270	302	367	596			

Butyric Acid.

100 $p_1$ .....	0	29.5	49	68.2	74.6	82.2	89.1	100	
$10^4 \rho$ .....	9982	10060	9986	9933	9889	9856	9779	9652	
$10^3 \eta$ .....	1003	2186	3091	3560	3576	3404	3015	1555	
$-x_1/\rho_2 - x_2/\rho_1$ ..	...	217	207	228	250	296	379		

This table comprises a helpful range of facts. While formic acid shows no maximum of viscosity, acetic acid has a marked maximum at the same value of  $p_1$  as gives a

maximum of density, and propionic and butyric acids show a decided maximum of viscosity at a value of  $p_1$  different from that of maximum density. The viscosity of mixtures of water and formic acid is nearly given by the simple mixture formula, and the fluidity also, so  $1/\eta - p_1/\eta_1 - p_2/\eta_2$  is small and negative and of the same order of magnitude as  $(p_1/\eta_1 + p_2/\eta_2)\rho\Delta$ , so that  $x_1/\rho_2 + x_2/\rho_1$ , which stands for

$$\{1/\eta - p_1/\eta_1 - p_2/\eta_2 - (p_1/\eta_1 + p_2/\eta_2)\rho\Delta\}/p_1p_2\rho$$

has small values for formic acid compared with those for the other acids. For acetic acid and water the tabulated results can be expressed by

$$\left. \begin{aligned} \{1/\eta - p_1/\eta_1 - p_2/\eta_2 - (p_1/\eta_1 + p_2/\eta_2)\rho\Delta\}/p_1p_2\rho &= -169 \\ &\text{from } p_1=0 \text{ to } 0.5 \\ &= -169 - 1150(0.25 - p_1p_2) \\ &\text{from } p_1=0.5 \text{ to } 1 \end{aligned} \right\} \quad (35)$$

$$\left. \begin{aligned} \text{Retaining the same forms, we can write for formic acid} \\ &= -13 \quad \text{from } p_1=0 \text{ to } 0.5 \\ &= -13 + 50(0.25 - p_1p_2) \\ &\text{from } p_1=0.5 \text{ to } 1 \end{aligned} \right\} \quad (36)$$

$$\left. \begin{aligned} \text{for propionic acid} &= -209 \quad \text{from } p_1=0 \text{ to } 0.5 \\ &= -209 - 2040(0.25 - p_1p_2) \\ &\text{from } p_1=0.5 \text{ to } 1 \end{aligned} \right\} \quad (37)$$

$$\left. \begin{aligned} \text{and for butyric acid} &= -210 \quad \text{from } p_1=0 \text{ to } 0.5 \\ &= -210 - 900(0.25 - p_1p_2) \\ &\text{from } p_1=0.5 \text{ to } 1 \end{aligned} \right\} \quad (38)$$

These equations show a certain similarity of form to those for  $(\Delta + \rho\Delta^2/2)/p_1v_2\rho$  for the fatty acids. The maximum contraction with formic acid is only about half the maximum with acetic acid. Yet with half the contraction there is hardly any departure from the simple mixture rule for viscosity or fluidity in formic acid and water. This fact suggests that there are two opposite tendencies as regards the connexion between contraction and change of fluidity, the one increasing fluidity beyond that given by the simple mixture rule, the other decreasing it. In formic acid the contraction goes so far that these two tendencies almost neutralize one another, so that in spite of the contraction on mixing formic acid and water, the resulting fluidity is the same as if the liquids mingled like a pair of ordinary non-associating liquids. This fact confirms the suggestion

offered above in connexion with alcohol and water to account for the fact that the reduction of viscosity which ought to accompany the change of trihydrol into dihydrol does not appear, that it is masked by a greater increase of viscosity of mutual origin. With formic acid this increase of mutual origin is almost equal to the decrease, and so as regards viscosity, formic acid and water behave almost as if no molecular changes were going on at all. On the other hand, the other acids, like alcohol, show the increase of viscosity preponderating over the decrease and producing the conspicuous maximum. The two equations for the fluidity of each acid are further evidence for the two processes when these acids are mixed with water, first a change of trihydrol into dihydrol along with production of hydrol, and second a process which is chiefly production of hydrol. In "The Mol. Const. of Solutions" it is shown that most electrolytic solutes change trihydrol into dihydrol and therefore produce contraction on solution. But they generally produce increase of viscosity. Probably with them also there is an increase in the mutual part of the viscosity which is greater than the decrease due to change of trihydrol into dihydrol. Probably the chief reason for the difference of the action of formic acid from that of the other acids is the closer approach of its dielectric capacity to that of water.

*Specific Heat ; Heat evolved on mixing.*

Dupré and Page (Phil. Trans. clx. p. 591, 1869) found that a mixture of alcohol and water containing 20 per cent. of alcohol has a specific heat 1.044, although that of alcohol is 0.604, a result which led them to investigate the specific heat and other physical properties of such mixtures systematically. They discovered that the heat evolved on mixing alcohol and water is proportional to the change of specific heat which occurs on mixing. This remarkably simple relation between heat evolved and change of a physical property was not verified by Winkelmann (Pogg. Ann. cl. p. 592, 1873), who obtained values for the heat evolved agreeing well with those of Dupré and Page, but values for the change of specific heat diverging from those of Dupré and Page with increasing percentage of alcohol. At first then we shall use quite recent data for the specific heat of mixtures of alcohol and water, namely those of Bakowski (*Ann. d. Phys. Beibl.* xxxiii. p. 858, 1909) between 22° and 99° C. He summarises his results in the following

*Phil. Mag.* S. 6. Vol. 22. No. 127. July 1911, F

formulæ with the mean specific heat of water between  $22^{\circ}$  and  $98^{\circ}$  taken as unity :—

$$c = 0.6628 + 0.7945p_2 - 0.45p_2^2 \quad \text{from } p_2 = 0 \text{ to } 0.5 \quad (39)$$

$$= 0.9475 + 0.5164(p_2 - 0.5) - 0.625(p_2 - 0.5)^2 \\ \text{from } p_2 = 0.5 \text{ to } 0.8 \quad (40)$$

$$= 1.0455 - 0.104(p_2 - 0.7991) - 0.482(p_2 - 0.7991)^2 \\ \text{from } p_2 = 0.8 \text{ to } 1.0 \quad (41)$$

From these we derive the following values of  $c - p_1c_1 - p_2c_2$  the increase of specific heat on mixing, with  $c_1 = 0.6628$  and  $c_2 = 1$ , namely

$$0.4573p_2 - 0.45p_2^2 \text{ or nearly } 0.458p_1p_2 \quad \text{from } p_2 = 0 \text{ to } 0.5$$

$$0.446p_1p_2 - 0.179p_1^2 + 0.049 \quad \text{from } p_2 = 0.5 \text{ to } 0.8$$

$$0.482p_1p_2 + 0.153p_1 + 0.005 \quad \text{from } p_2 = 0.8 \text{ to } 1.0$$

It will be noticed that in each case the most important term is nearly  $0.45p_1p_2$ , a result which, by itself, would make it appear that there is only one main process in the reaction between alcohol and water. At the limit when  $p_2$  is small we have

$$(c - p_1c_1 - p_2c_2)/p_2 = 0.458p_1 = 0.458.$$

But if in this case  $p_2$  water is changed into  $p_2$  hydrol of specific heat  $c_2'$ , we can write the last expression

$$(c - p_1c_1 - p_2c_2' - p_2c_2 + p_2c_2')/p_2,$$

in which, by the simple mixture formula,

$$c - p_1c_1 - p_2c_2' = 0,$$

so that the expression becomes

$$c_2' - c_2 = 0.458, \quad \text{and} \quad c_2' = 1.458.$$

But at the Faraday Society's discussion I found 0.513 to be the average specific heat of solid hydrol as water of crystallization. It appears then that  $c_2'$  is only hypothetically a specific heat of hydrol to which the simple mixture formula applies, that it includes both the specific heat of hydrol and the rate of change of its heat of solution in alcohol with temperature. At the other limit when  $p_1$  is small and  $p_2$  nearly 1,

$$(c - p_1c_1 - p_2c_2)/p_2 = 0.635p_1 + 0.005(1 + p_1),$$

where the difference between 0.640 and 0.458 indicates a certain difference between the reactions at the two limits, but not a very pronounced one. The specific heat of dihydrol

is 0·8 and of trihydrol 0·6, so that the change of trihydrol into dihydrol causes on that account a decrease of specific heat. But the rate of change of the remaining trihydrol may be affected and the heat of solution of the mixed trihydrol and dihydrol may also be changed. Thus, notwithstanding the one known cause of a reduction of specific heat when a little alcohol is added to water, the total result is an increase, which in the limit when  $p_1$  is small amounts to  $0·640p_1$  neglecting 0·005. From the data of Winkelmann at 0° C. I have obtained the equations

$$\left. \begin{aligned} c - p_1c_1 - p_2c_2 &= 0·78p_1p_2 && \text{from } p_2 = 1 \text{ to } 0·8 \\ &= 0·78p_1p_2 - (0·8 - p_2)p_1p_2 && \text{from } p_2 = 0·8 \text{ to } 0·5 \\ &= 0·33p_1p_2 + 0·5(p_2 - 0·2)p_1p_2 && \text{from } p_2 = 0·5 \text{ to } 0·2 \\ &= 0·33p_1p_2 && \text{from } p_2 = 0·2 \text{ to } 0 \end{aligned} \right\} (42)$$

Thus  $(c - p_1c_1 - p_2c_2)/p_2$ , when  $p_2$  is nearly 1, has the limiting value  $0·640p_1$  nearly at 60° C. and  $0·78p_1$  at 0°, while when  $p_2$  is small the value is  $0·458$  at 60° C. and  $0·33$  at 0°. The opposite changes with temperature at these two limits are further evidence that there are two main reactions of alcohol on water. The data of Dupré and Page at about 17° C. make the large limit a little larger and the smaller limit smaller than the values just given from Winkelmann's, but they confirm the result that the change with temperature at the two limits takes place in opposite directions. As the experiments of Winkelmann are of later date and carried out as a check on those of Dupré and Page, it is necessary to take as disproved the remarkable conclusion of Dupré and Page that the heat evolved on mixing is proportional to the change of specific heat. But as the values found for the heat evolved agree well in the two sets of experiments, these can be investigated on an assured basis. The following table gives Winkelmann's values for H, the heat evolved in forming 1 gramme of mixture at 0° C., and also  $H/p_1p_2$  :—

100 $p_1$ .....	10	20	30	40	50	60	70	80	90
10 H .....	64	107	120	110	91	71	52	33	18
H/ $p_1p_2$ .....	71	67	57	46	36	30	25	21	20

It appears that  $H/p_1p_2$  tends towards a limit near 70 when  $p_2$  is 1, and towards a limit about 20 when  $p_2$  is small, its values for intermediate cases being expressible by simple linear forms. The difference between the two limits is great enough to confirm the idea that they belong to two different

reactions of alcohol upon water. I find with the data of Winkelmann that the following empirical relation takes the place of the simpler one of Dupré and Page:

$$H = 95(c - p_1c_1 - p_2c_2) - 5(\rho - p_1\rho_1 - p_2\rho_2) \quad . \quad . \quad (43)$$

For the first four fatty acids the data for  $c$  and  $H$  were obtained by Lüdeking (Wied. *Ann.* xxvii. p. 72, 1886),  $c$  between  $50^\circ$  C. and  $20^\circ$ . Ignoring some marked peculiarities at certain values of  $p_1$ , we can summarise the experimental results for  $c$  in the following statement:—

<i>Acid.</i>	$c - p_1c_1 - p_2c_2$	from $p_1 =$	to $p_1 =$
Formic .....	0.0569	0.836	0.836
	0.0297	0.719	0.719
	$-0.03 p_1 p_2$	0.630	0.389
	$-0.07 p_1 p_2$	0.338	0.242
	$-\{0.07 + 0.8(0.242 - p_1)\} p_1 p_2$	0.242	0.0
Acetic.....	$-0.0074$	0.869	0.869
	$0.08 p_1 p_2$	0.769	0.625
	$0.12 p_1 p_2$	0.526	0.250
	$\{0.12 + 0.7(0.25 - p_1)\} p_1 p_2$	0.250	0.0
Propionic .....	0.16	0.891	0.891
	$0.25 p_1 p_2$	0.804	0.406
	$\{0.25 + 0.2(0.406 - p_1)\} p_1 p_2$	0.406	0.0
Butyric .....	$\{0.35 - 0.4(0.907 - p_1)\} p_1 p_2$	0.907	0.379
	$\{0.15 + 0.2(0.379 - p_1)\} p_1 p_2$	0.379	0.0

Formic acid stands apart from the others by having  $c - p_1c_1 - p_2c_2$  negative except for the two highest values of  $p_1$  where it assumes a large positive value. In all other cases  $c - p_1c_1 - p_2c_2$  is positive except at the highest value of  $p_1$  for acetic acid. The distinction between formic and the other acids recalls the fact that  $\Delta$  is smaller for formic acid than the others. The limit of  $(c - p_1c_1 - p_2c_2)/p_1p_2$  for small values of  $p_2$  is not obtainable from these experiments. When  $p_2 = 1$  it seems to be about  $-0.26$  for formic,  $0.3$  for acetic,  $0.3$  for propionic, and  $0.2$  for butyric acid. These limits indicate similar reactions for the three latter acids upon an excess of water. The facts all point to more than one action, but the conditions are so complicated that it is not possible at present to demonstrate two main processes, that of change of trihydrol into dihydrol and that of change of dihydrol into hydrol. The chief complication is the heats of solution of the varying amounts of hydrol, di- and trihydrol in the different acids.

The values of  $H$  run characteristic courses with the four acids. With formic acid  $H$  is positive except for a small region of  $p_1$  near  $0.1$  and attains a maximum value of  $2.14$

calories per gramme of mixture when  $p_2=0.72$ . For the other three acids  $H$  is for the most part negative; that is, there is an absorption of heat on mixing, except that when  $p_1=0.18$  for acetic,  $0.17$  for propionic, and  $0.10$  for butyric acid,  $H$  becomes positive and remains positive for smaller values of  $p_1$ . Here we meet a similar contrast between formic acid and the others to that we found in  $c-p_1c_1-p_2c_2$ . I have found the following empirical relation to hold for the four acids as well as for alcohol except when  $p_1=0.836$  for formic and  $0.869$  for acetic acid:

$$H - a(c - p_1c_1 - p_2c_2) = b(\rho - p_1\rho_1 - p_2\rho_2) \quad . \quad . \quad (44)$$

with the following values for  $a$  and  $b$  :—

<i>Acid...</i>	Formic.	Acetic.	Propionic.	Butyric.	Alcohol.
$a$ .....	30	--50	--140	--210	--95
$b$ .....	76	--83	--396	--549	--5

It will be noticed that the successive differences in  $a$  for the acids are 80, 90, and 70, while for  $b$  they are 159, 313, and 153. Thus the formula (44) links up the complicated phenomena for the four acids and alcohol in a way that shows the chemical structure of the substance added to water to have a definite influence on the energy changes it produces in the water, for I take the term  $b(\rho - p_1\rho_1 - p_2\rho_2)$  to be a rough measure of a change of potential energy. For the general study of potential energy in our mixtures we would need a kinetic theory of liquids. With surface energy, measured by surface tension, we can make some progress at once.

### *Surface Energy.*

In "The Mol. Const. of Water" it is shown that from  $0^\circ$  C. to  $40^\circ$  the surface film of water in contact with air or its own vapour consists of trihydrol. There is evidence that at temperatures above  $60^\circ$  the diminution of the surface tension allows some dihydrol to exist in the surface layer. At temperatures near  $15^\circ$  C. then in the surface layer the problems of surface tension reduce to those of a binary mixture, unless the substance added to water has the power of transforming the trihydrol of the surface film into dihydrol or hydrol. The best and simplest assumption to begin with is that in the surface of a mixture the tension enables the trihydrol to exist just as in the surface of pure water. If this assumption were sufficient, then the surface tension of our mixtures would not be exceptional, it would conform to the

rules for surface tension in normal mixtures. But it is well known that the surface tension of mixtures of water with the alcohols and fatty acids is exceptional. The abnormality increases with increasing molecular weight of alcohol and acid, for instance, while water has a surface tension 71 dynes/cm. and isoamyl alcohol 24, a mixture containing 2 per cent. of isoamyl alcohol has a surface tension 30, almost that of the pure alcohol, while  $2\frac{1}{2}$  per cent. of isovaleric acid reduces the surface tension of water to 36, that of the pure acid being 26. Probably then isoamyl alcohol and isovaleric acid are far more concentrated in the surface film than in the bulk of the mixtures. Similar causes to those which convert the water of the bulk into trihydrol produce a higher concentration of the alcohols and fatty acids in the surface of mixtures than in the bulk. So we shall now investigate the ratio  $p_{1s}/p_1$  of concentration in the surface film to that in the bulk. The fundamental equation for the surface tension  $\alpha$  of a mixture is (Phil. Mag. (6) xx. p. 262, 1910)

$$\alpha/\rho^2 = (p_1\alpha_1^{\frac{1}{2}} + p_2\alpha_2^{\frac{1}{2}})^2 \quad . \quad . \quad . \quad (45)$$

With  $p_1 + p_2 = 1$  this becomes an equation for finding  $p_1$  as  $p_{1s}$  the value in the surface film when the  $\alpha$ 's and  $\rho$ 's are known. The surface tensions of mixtures of water with alcohols and fatty acids from 15° C. to 20° have been measured by Traube (*Journ. f. prakt. Chem.* xxxiv. p. 292, 1886; *Ann. der Chem.* cclxv. 1891). At each temperature  $\alpha_2$  for water is  $\alpha_2$  for trihydrol 72 dynes/cm. at 15° and 71.7 at 20° according to Traube's data, while  $\rho_2$  at 0° is about 0.88, say 0.877 from 15° to 20°. For ethyl alcohol at 17.5

$$\alpha_1 = 22.0 \quad \text{and} \quad \rho_1 = 0.7906.$$

From his data for  $\alpha$  and  $\rho$  the following values of  $p_{1s}/p_1$  have been calculated:—

100 $p_1$ .....	10	20	30	40	50	60	80
	3.90	2.91	2.36	1.95	1.66	1.435	1.15

A mixture of ethyl alcohol and water containing 10 per cent. of alcohol in the bulk has a strength of 39 per cent. in the surface film. These ratios can be expressed by the formula

$$p_1/p_{1s} = 0.165 + 0.88 p_1 \quad . \quad . \quad . \quad (46)$$

with a maximum error of 1.2 per cent. when  $p_1 = 0.3$ . This simple formula shows how alcohol is distributed between water in the bulk and trihydrol in the surface, when  $p_1$  has values between 0.1 and 0.8.



The interesting limiting case when  $p_1$  is nearly 1, when water is added to a large excess of alcohol, has not, to my knowledge, been studied experimentally. It might show the trihydrol in the film being changed by the alcohol. If (46) is carried to the limit  $p_1=1$  it makes  $p_{1s}/p_1=0.96$ , which is near enough to 1 to show that probably (46) holds nearly up to  $p_1=1$ . At the other limit when  $p_1$  is less than 0.1 equation (46) begins to fail. Down to Traube's lowest  $p_1$ , namely 0.00288, the following equation holds from  $p_1=0.068$ :

$$p_1/p_{1s}=0.88 p_1 + 0.235 + 0.06 \log_{10} p_1. \quad (47)$$

For acetic acid and water the equations corresponding with (46) and (47) are with a maximum error of 4 per cent.:

$$p_1/p_{1s}=0.195 + 0.93 p_1 \quad \text{when } p_1 > 0.35 \quad (48)$$

$$=0.93 p_1 + 0.220 + 0.055 \log_{10} p_1 \quad \text{when } p_1 < 0.35 \quad (49)$$

These equations may be written

$$p_1/p_{1s}=a + b p_1 \quad \text{when } p_1 > g \quad (50)$$

$$=b p_1 + c + f \log_{10} p_1 \quad \text{when } p_1 < g, \quad (51)$$

values of  $a$ ,  $b$ ,  $c$ ,  $f$ , and  $g$  being gathered in the next table.

<i>Alcohol:</i>	$a$	$b$	$c$	$f$	$g$
Methyl .....	0.334	0.77	0.390	0.08	0.2
Ethyl .....	0.165	0.88	0.235	0.06	0.07
Propyl .....	0.04	0.97	...	...	...
Isobutyl .....	0.019	0.87	...	...	...
Isoamyl .....	0.007	0.90	...	...	...
<i>Acid:</i>					
Formic .....	0.322	0.86	0.417	0.14	0.21
Acetic .....	0.195	0.93	0.220	0.055	0.35
Propionic.....	0.071	1.03	0.084	0.0167	0.17
Butyric.....	0.009	1.03	0.0217	0.0066	0.01
Isobutyric ....	0.012	1.00	0.0217	0.0066	0.03
Isovaleric.....	0.0123	0.81	0.0206	0.0050	0.02

The values of  $b$  all lie between 0.77 and 1.03. Alcohol and acid containing the same number of carbon atoms in the molecule have nearly equal values of  $a$  and also of  $c$ , these diminishing rapidly with increasing number of carbon atoms in the molecule. Here we have evidence of an interesting relation between molecular structure and the relations of these alcohols and acids to trihydrol under surface tension.

If we take  $b$  to be 1 and  $a$  to be negligible, then (50) makes  $p_{1s}=1$ , the limiting case for the higher alcohols and

acids which on being added to water form a surface film of their own pure substance. This remarkable tendency amongst the alcohols and fatty acids confirms the theoretical deduction that the surface film of water at low temperatures from  $0^{\circ}\text{C.}$  to  $40^{\circ}$  consists of trihydrol. Otherwise this investigation of the exceptional surface tensions of our mixtures does not advance the immediate subject of our inquiry except that it shows a contrast between the simple course of the equation (50) applying over a wide range of  $p_1$  to the pure trihydrol of the surface film and the frequently double course of the equations required to express the changes of other properties in the bulk consisting of both trihydrol and dihydrol.

#### 4. *Conclusions to be drawn from these Results.*

In the study of contraction it was found that its course in mixtures of water and alcohol could be fairly well separated into two processes, that of conversion of the trihydrol of water into dihydrol, which is completed when the percentage of alcohol has risen to 46. At this point the experimental contraction is 0.0408, and that calculated from conversion of trihydrol into dihydrol 0.0393. When  $p_1$  is 0.46, the contraction gives 0.873 for the density of liquid trihydrol in place of 0.88 deduced from the density of ice. When  $p_1$  is 0.99 and  $p_2$  is 0.01 the contraction for the change of 0.01 water into hydrol of density 1.26 would be 0.00206, while the experimental contraction is 0.00230. In other words the hydrol produced by alcohol would need to have a density 1.31 in place of 1.26 deduced for liquid hydrol from the density of solid hydrol in water of crystallization. With acetic acid and water contraction does not proceed so rapidly with increasing amount of acid as in the case of alcohol. Both processes seem to go on together. But when  $p_2$  is small the contraction is such as would give a density 1.443 to hydrol instead of 1.26.

This confronts us with the difficulty of having to regard hydrol as a highly variable substance. When we turn to the case of 0.01 water in 0.99 of formic acid, we find a contraction only half of that occurring with 0.99 of acetic, propionic, and butyric acid. All through, the action of formic acid on water is less vigorous than that of the next three fatty acids. With formic, propionic, and butyric acids the experimental data for small enough values of  $p_2$  are lacking to enable us to ascertain whether the density of hydrol in an excess of these acids is the same as in excess

of acetic acid. The exceptional behaviour with formic acid is traced to its dielectric capacity's having a value 60 near to the 80 of water. Molecules of water in formic acid are nearly in the same electrical environment as in water, whence the less vigorous action of formic acid. On the whole, the available data for propionic and butyric acids corroborate those for acetic acid, though, so far as they go, they indicate for hydrol the same sort of density as those for alcohol.

As regards refraction the value of  $(n_2^2 - 1)/(n_2^2 + 2)\rho_2$  for water as a changing substance is calculated from the values for mixtures of water and alcohol on the assumption that alcohol is an unchanging substance. As the amount of alcohol increases from 0 to  $p_1 = 0.5$ , the values diminish to a minimum, in qualitative agreement with the fact that  $(n^2 - 1)/(n^2 + 2)\rho$  has a smaller value for dihydrol than for trihydrol. The minimum value 0.20733 is not so small as 0.20674 for pure dihydrol, so that the optical results do not fully confirm our conclusion from contraction that the change from  $p_1 = 0$  to  $p_1 = 0.5$  may be considered to consist almost wholly of change of trihydrol into dihydrol. Indeed with the contraction it appeared that rather more contraction occurs than is accounted for solely by change of trihydrol into dihydrol, perhaps a little change to hydrol having occurred. With the optical results we can suppose the difference between 0.20733 and 0.20674 to be accounted for by change of a little dihydrol into hydrol having a larger  $(n^2 - 1)/(n^2 + 2)\rho$ . Beyond  $p_1 = 0.5$  the results show that, if hydrol is produced, it must have  $(n^2 - 1)/(n^2 + 2)\rho$  larger than for dihydrol. But in water of crystallization  $(n^2 - 1)/(n^2 + 2)\rho$  has a value only  $\frac{3}{4}$  that for dihydrol. On the other hand, in vapour of water this has for hydrol a value 0.3 per cent. greater than for dihydrol. Here we encounter again the difficulty that hydrol is a substance of variable properties, a fact which I would ascribe to the variable electric moment of the doublet  $\#b$  latent in its oxygen atom. Hydrol in excess of alcohol has a value between 0.2107 and 0.2110 for  $(n^2 - 1)/(n^2 + 2)\rho$  and in vapour of water the value 0.2092. In excess of acetic acid it is 0.2101. In the case of acetic acid  $(n_2^2 - 1)/(n_2^2 + 2)\rho_2$  with increasing  $p_1$  reaches a minimum when  $p_1 = 0.25$ , a result in harmony with the view that with acetic acid the changes of trihydrol into dihydrol and of dihydrol into hydrol occur concurrently. On the whole then the optical results confirm the theory advanced to account for contraction.

With  $(K - 1)/\rho$  for mixtures of water and alcohol we

found the results consistent with the idea that when  $p_1$  is less than 0.5 alcohol changes the trihydrol of water into dihydrol, and when  $p_1$  is greater than 0.5, dihydrol is changed into hydrol, which in the experiments of Abegg has a dielectric capacity equal to that of dihydrol, in those of Nernst less and in those of Thwing still less. In the solid hydrol of water of crystallization K is much less again, being of the order of magnitude of 6. In Thwing's experiments with acetic acid and water K for hydrol and  $(K-1)/\rho$  appear to be larger than for dihydrol. Here again we have evidence that the properties of hydrol are very variable with environment. From the study of fluidity we get good evidence of molecular changes, probably two main changes, but the alterations of fluidity involve changes of the mutual relations of unlike molecules in contact as well as changes of individual properties caused by change of molecular constitution. A kinetic theory of the viscosity is needed for interpreting the experimental results definitely.

In interpreting the change of specific heat on mixing we encounter the same difficulty, that there are changes of mutual relation as well as of individual property. In mixtures of alcohol and water the change of specific heat occurs nearly as if it were caused by only a single molecular change,  $(c-p_1c_1-p_2c_2)/p_2$ , at 60° C., ranging nearly from  $0.640 p_1$  to  $0.458 p_1$  as  $p_1$  passes from 0 to 1. At 0° the corresponding range is from  $0.78 p_1$  to  $0.33 p_1$ , this contrast supplying evidence that probably here there are two main molecular changes really occurring. With the heat H evolved on making a gramme of mixture it is found that  $H/p_1p_2$  tends to two different limits 70 and 20 when  $p_1=0$  and 1. From the specific heats of mixtures of water with the fatty acids no definite conclusions are drawn. The surface energy of mixtures is investigated from the point of view that the surface of water below 40° C. consists of trihydrol and the surface of a mixture of trihydrol and the other ingredient in different proportions from those of the bulk. Simple relations are thus obtained for  $p_{1s}/p_1$ , but the results do not bear directly on our problems of the molecular constitution of the mixture in the bulk.

It is fairly well established that at ordinary temperatures the liquid alcohols and fatty acids have molecules double of those represented by their usual chemical formulas. Throughout the present discussion it has been assumed that on mixing with water these molecules are unchanged, the ionization of the fatty acids having a negligible effect on

the physical properties at the concentrations we have been studying. Even in fairly dilute solutions, such as 1 per cent., alcohol exists as  $(C_2H_5OH)_2$  and acetic acid as  $(CH_3COOH)_2$ . Yet by the method of the lowering of the freezing-point it has been accepted as proved that in such solutions alcohol and acetic acid exist as  $C_2H_5OH$  and  $CH_3COOH$ . I think that the method of the lowering of the freezing-point fails here to give the whole molecular weight and yields the weight of the nearly free halves of the double molecules. According to the theory of the present paper it is assumed on the contrary that the trihydrol and dihydrol of water in excess of the alcohols and fatty acids are converted into hydrol consisting of single molecules of  $H_2O$ . But water in all solvents at small concentrations gives only molecules of the form  $H_2O$  (the latest reference is that of Walden to Bruni & Amadori, Trans. Faraday Soc. v. 1910). For the reason just given we cannot accept this as proof that water at low concentrations in other solvents exists as hydrol, because the methods hitherto used involve the assumption objected to in that of the lowering of the freezing-point. At all events, I can discover no evidence against the view that in a dilute solution of water in alcohol and in acetic acid the water is changed into hydrol, as in the vapour of water.

According to the principles of the present paper, the ionization of weak electrolytes takes a new aspect. If the two groups in  $(CH_3COOH)_2$  are so nearly free that each acts as if free in the lowering of the freezing-point of a solvent, then in that solvent the conditions are favourable to the occurrence of dissociation amongst the double molecules according to the laws of probability. It is to be expected then that at infinite dilution in water alcohol  $(C_2H_5OH)_2$  is dissociated into  $C_2H_5OH$ . To follow the process there would need to be very accurate measurement of the physical properties of dilute solutions of alcohol. In the case of the acids the single molecule like  $CH_3COOH$  is ionized into ions like  $H^\#$  and  $CH_3COO^\flat$ , and electrical methods of easy application become available for studying the changes taking place. It appears that the double molecule of the fatty and other organic acids is not an electrolyte, but that the single dissociated molecule is an electrolyte. To it applies the principle which I have stated for electrolytes in general, that their ionization is always complete. Hence in a dilute solution of acetic acid the equilibrium is between  $(CH_3COOH)_2$  on the one hand and  $H^\#$  and  $CH_3COO^\flat$  on the other. The

degree of ionization of a weak electrolyte in the definition of van 't Hoff, Arrhenius, and Ostwald is really a measure of the dissociation of its double molecules and of the ionization of the single molecules resulting therefrom. For these reasons the electrical conductivity of solutions of the fatty acids will receive special study in the next section.

### 5. *Electric Conductivity of Solutions of the Fatty Acids.*

The fatty acids will be investigated here as typical weak electrolytes. Let a gramme-molecule (for a single molecule, such as  $\text{CH}_3\text{COOH}$  for acetic acid) be dissolved to make  $V$  litres of solution, and let the molecular conductivity of the solution as hitherto defined be  $\lambda$ , and its viscosity be  $\eta$ ,  $\lambda_0$  and  $\eta_0$  being the values when  $V$  is infinite. Then, according to the usual notation of Ostwald's theory for weak electrolytes  $\lambda/\lambda_0 = \alpha$  or  $i$  the degree of ionization. As a rule the investigation is confined to values of  $V$  so large that it may be assumed that  $\eta = \eta_0$ . It is better to provide for a difference between  $\eta$  and  $\eta_0$  by writing  $\lambda\eta/\lambda_0\eta_0 = \alpha$  or  $i$ . The simple theory of Ostwald is that the non-ionized electrolyte  $1 - \alpha$  is ionized at a rate  $k(1 - \alpha)/V$ , and that the two sets of ions recombine at a rate  $k'\alpha^2/V^2$ , so that for equilibrium

$$k(1 - \alpha)/V = k'\alpha^2/V^2 \quad \therefore \alpha^2/(1 - \alpha)V = k/k' = K. \quad (52)$$

This is the equation which is in beautiful accord with the experimental facts,  $10^6K$  having the following values near  $15^\circ \text{C}$ ., those of  $\lambda_0$  at  $18^\circ$  being added from the data of Kohlrausch.

<i>Acid ...</i>	<i>Formic.</i>	<i>Acetic.</i>	<i>Propionic.</i>	<i>Butyric.</i>	<i>Isobutyric.</i>	<i>Valeric.</i>	<i>Caproic.</i>
$10^6K \dots$	214	18	13	15	14	16	14
$\lambda_0 \dots$	365.2	353.4	349.8	346.3	...	...	...

For dilute solutions of the fatty acids, then, we have

$$(\lambda\eta/\lambda_0\eta_0)^2 = KV(1 - \lambda\eta/\lambda_0\eta_0). \quad . \quad . \quad . \quad (53)$$

I propose to give a different interpretation to this formula from that current in the text-books of physical chemistry after Ostwald, van 't Hoff, and Arrhenius. It is important then first to pass to the case of solutions which are not dilute. With acetic acid between  $p_1 = 0.4$  and  $p_1 = 0.9$ , Grunmach (*Ann. d. Phys.* [4] xxviii. p. 217, 1909) noticed that  $\lambda^{\frac{1}{2}}$  is nearly linear in the concentration  $\rho p_1/M_1 = 1/10^3V$ . With this clue I have found that in not dilute solutions of the first four fatty acids  $(\lambda\eta)^{\frac{1}{2}}$  is linear in  $p_1$ . To illustrate this

relation we can use the data of Otten from the *Tabellen* for  $\lambda$  at 18° C. for formic acid and propionic acid, using for  $\eta$  the values found by Tsakalotos at 20°, which in the case of water differ by about 2 parts in 1000 from the mean of the best experimental values at 18°. For formic acid

$$(\lambda\eta)^{\frac{1}{3}} = 0.3308 - 0.2386 p_1 \quad . \quad . \quad . \quad (54)$$

as shown by the comparison

$10^4 p_1$ .....	955	2034	2983	3995	5002	5996	7006	8902	9853
$10^4 (\lambda\eta)^{\frac{1}{3}}$ exp. ...	3346	2863	2599	2343	2116	1884	1638	1107	572
„ calc. ...	3080	2823	2597	2355	2114	1877	1636	1184	957

For propionic acid

$$(\lambda\eta)^{\frac{1}{3}} = 0.2217 - 0.223 p_1, \quad . \quad . \quad . \quad (55)$$

the comparison being

$10^4 p_1$ .....	1007	2001	3004	5004	7001	8997	10000
$10^4 (\lambda\eta)^{\frac{1}{3}}$ exp. ...	2190	1820	1542	1086	626	347	180
„ calc. ...	1992	1770	1547	1100	656	185	-13

The case where  $p_1=1$  does not rightly enter into the comparison, it is added for information only.

For acetic acid with the data of Kohlrausch

$$(\lambda\eta)^{\frac{1}{3}} = 0.2366 - 0.223 p_1, \quad . \quad (56)$$

and for butyric acid with the data of Otten

$$(\lambda\eta)^{\frac{1}{3}} = 0.2376 - 0.245 p_1. \quad . \quad (57)$$

For propionic acid (55) can be simplified to

$$(\lambda\eta)^{\frac{1}{3}} = 0.225 p_2, \quad . \quad . \quad . \quad (58)$$

and for butyric (57) to the same. Our essential theoretical problem is to interpret the meaning of the simple form  $(\lambda\eta)^{\frac{1}{3}} = ap_2$  in a manner harmonious with the interpretation of (53). It becomes  $(\lambda\eta/\lambda_0\eta_0)^2 = a^6 p_2^6 / \lambda_0^2 \eta_0^2$  which may be regarded as an approximation derived from

$$(\lambda\eta/\lambda_0\eta_0)^2 = a^6 p_2^6 \rho^6 (1 - \lambda\eta/\lambda_0\eta_0) / \lambda_0^2 \eta_0^2, \quad . \quad . \quad (59)$$

in which  $\lambda\eta/\lambda_0\eta_0$  is small. It may be said that (53) in the fatty acids holds from  $p_1=0$  nearly, to 0.1, and (58) from 0.2 to 0.8 or 0.9, a transition form being required for values of  $p_1$  between 0.1 and 0.2. When  $p_1=0.2$ ,  $\lambda\eta/\lambda_0\eta_0$  has a value about 0.006 for formic acid and 0.002 for the others. We can now interpret (59) and (53) together.

If there are  $a$  double molecules per unit volume, of which  $x$  are ionized, there are  $2x$  ions of each sort uniformly

distributed through unit volume. On the average these may be assumed to be at the angles of a division of the unit volume into  $2x$  equal cubes. A typical sample set of these neighbour pairs of ions for acetic acid may be represented by the large square ABCD, and by the small square abcd if they have re-combined to form a double molecule. This re-combination might be a quadruple event resulting from the four independent incidents of the journey of A to a and so on, in which case its probability would be proportional to  $x^4$ . But it may be that there needs only a favourable conjunction of the pair AB with the pair DC to cause recombination, so that, as there are  $2x$  of such pairs, the probability of recombination will be proportional to  $x^2$ . From the empirical success of the formula known as Ostwald's dilution law, we conclude that the probability is proportional to  $x^2$  and not to  $x^4$ , unless indeed the rate of dissociation were proportional to  $(a-x)^2$ , in which case the probability measured by  $x^4$  would lead to that formula. I shall assume that in dilute solutions the rate of dissociation is proportional to  $a-x$ , and that of recombination to  $x^2$ .

Turning to solutions which are not dilute as regards double molecules we can interpret (59) as a more general form of the relation

$$x^2 = k'(a-x)/k \text{ or } (\lambda\eta/\lambda_0\eta_0)^2 = K(1-\lambda\eta/\lambda_0\eta_0)M_1/p_1\rho. \quad (60)$$

Apparently then  $k'/k$ , instead of being a constant in (59) takes the form  $a^6(p_2\rho)^6 p_1\rho/M_1\lambda_0^2\eta_0^2$  which causes  $p_1\rho$  to disappear from the equation. This implies that  $(a-x)^2$  in the general case takes the place of  $a-x$  in the special case of dilute solutions. The form  $(p_2\rho)^6(a-x)^2$  means that dissociation is brought about by a certain conjunction of six molecules of water with two double molecules of acid. No doubt other similar conjunctions promote dissociation, and the probability of dissociation is expressed by a series whose sum is equivalent to the probability of a conjunction of six molecules of water with two of acid in a position making the double molecules unstable. In the transition from one equation to the other  $(p_2\rho)^6 p_1\rho$  becomes constant. Disregarding  $\rho$  which does not vary much with  $p_1$ , let us find the value of  $p_1$  which makes  $(1-p_1)^6 p_1$  a maximum. It is  $p_1 = 1/7 = 0.143$ . We have already seen that the transition occurs at a value of  $p_1$  near this. The form  $(p_2\rho)^6 p_1\rho$  applies from  $p_1 = 0.8$  or  $0.9$  to  $p_1 = 0.143$  which makes it a maximum.



What occurs at the transition is this : as  $p_1$  diminishes below 0.143 and  $p_2$  increases above 0.857, the water molecules surround the double molecules of acid so freely and make destructive conjunctions with each separately so often, that the special conjunction of six molecules of water with two double molecules of acid sinks into comparative insignificance. Since in these theoretical considerations we have introduced  $\rho\rho$  the mass per unit volume, it is desirable to amend the equation (58) to the following form :

$$(\lambda\eta)^{\frac{1}{3}} = ap_2\rho, \quad . \quad . \quad . \quad . \quad . \quad (61)$$

in which  $a$  has the value 0.242 for acetic acid, 0.216 for propionic, and 0.235 for butyric. For formic acid the corresponding equation is

$$(\lambda\eta)^{\frac{1}{3}} = 0.254(p_2 + 0.25)\rho. \quad . \quad . \quad . \quad . \quad (62)$$

The close approach of 0.254, 0.242, 0.216, and 0.235 to equality is noteworthy, being due probably to the fact that in each case the formation of the double molecule is due to the junction of COO with COO by the bonds  $\#b$  between O atoms. It is interesting to notice that formic acid, which is exceptional for its large molecular conductivity in dilute solutions and its large  $K$  in Ostwald's formula, is also exceptional for its larger molecular conductivity in solutions which are not dilute and in having (62) in place of (61). This continuity in the exceptionality of formic acid confirms the theoretical attempt above to explain the nature of the continuity connecting the two types of equation for molecular conductivity. This continuity is evidence in support of the view that throughout the solutions of the fatty acids we have to do with double molecules. In the pure acids we have to do with such, probably therefore with a preponderance of such in their aqueous solutions containing 80 per cent. of acid. The nature of the continuity is most simply explained by the assumption that in an 80 per cent. solution of a fatty acid, as in its solutions of all other strengths, the molecules are all double. Otherwise, according to the current theory of weak electrolytes we need a law for the dissociation of the double molecules and a law for the ionization of the resulting single molecules. To give the broad similarities and simplicities we have just been discussing, these two laws would need to be brought into simple relations. In view of all the facts it seems to me that the better hypothesis is that the fatty acids in their aqueous solutions exist as double molecules, the Ostwald dilution formula giving the law of the equilibrium between the double molecules and the ions derived from

them. This is in other words the hypothesis which I suggested in discussing strong electrolytes, namely that water dissociates a certain number of double molecules into single molecules, which as strong electrolytes are immediately completely ionized, so that the solute is present only as double molecules and ions.

It is usually assumed that the molecular lowering of the freezing-point of water caused by acetic acid proves that the acid is present as single molecules. In 100 grammes of water 0.00571 of acetic acid give a molecular lowering of the freezing-point of  $2^{\circ}03$ , the normal being  $1^{\circ}85$ , 1.66 grammes give  $1^{\circ}86$ , 13.45 gr.  $1^{\circ}75$ , 25 gr.  $1^{\circ}63$ , 116.6 gr.  $1^{\circ}15$ . It is usually assumed that when 25 grammes of acetic acid are mixed with 100 of water, the greater part of the acid is dissociated into single molecules of which only a minute fraction are ionized. But in our examination of the physical properties of mixtures of water and acetic acid we have found no phenomena indicating that nearly up to  $p_1=0.25$  the greater part of the acetic acid undergoes one simple change. Almost all the evidence pointed to change in the water. The facts for the other fatty acids are similar. In the case of ethyl alcohol 86 grammes mixed with 100 of water give a molecular lowering of the freezing-point  $1.81$  degrees. We found no evidence in the physical properties of mixtures of water and alcohol to support the hypothesis that all the alcohol undergoes a simple change to the state of single molecules. The method of the molecular lowering of freezing-point for determining absolute molecular weights (masses) breaks down completely when applied to the delicate problem of the double molecules we are considering. This being so, there is no valid ground for assuming the existence of single molecules of the fatty acids in their aqueous solutions, and the current theory of weak electrolytes becomes virtually untenable. Its chief fault is that it draws attention away from the vastly important electric fields between an ion and its neighbour and therefore from the even more important ones in and around atoms. In Nernst's theory of the concentration cell one aspect of these fields is considered. In "Ionization in Solutions and Two New Types of Viscosity" and in "The Molecular Constitution of Aqueous Solutions" (Phil. Mag. [6] xiv. p. 1, 1907, xii. p. 1, 1906) I have sought to give due prominence to molecular and atomic electric fields. The two new types of viscosity have not made their appearance in the present discussion because with weak electrolytes the concentration of the ions is too small to bring in the viscosity

that has its origin in the mutual electric energy of neighbour ions. The other viscosity derived from the energy of ion and molecules of solvent is implicitly taken into account in the values of  $\lambda_0$  which it helps to determine. In all catalytic actions these electric fields must play a prime part. Take such an instance as the optimum strength of solution of HCl for the digestion of protein by pepsin. It looks very much as if this strength determined the best adjustment of electric fields between the ions of HCl to promote the catalytic action of the enzyme on the protein. In a similar way Emil Fischer's likening of the relation between enzyme and substrate to that between key and lock may perhaps be made more definite by replacing both key and lock by electric fields adjustable to one another in the manner of key and lock.

In the present section I have tried to bring the theoretical conception of the mode of action of weak electrolytes into line with the theory of strong electrolytes given in previous papers.

#### 6. Summary and General Conclusions.

Section 4 contains a summary of the part of the paper previous to it. In section 5 it is shown how Ostwald's dilution law for the molecular conductivity of weak electrolytes, such as the fatty acids, expresses the equilibrium between the double molecules and the ions of these acids in water. A formula  $(\lambda\eta)^{\frac{1}{3}} = ap_2p$  is developed for molecular conductivity in strong solutions (20 to 90 per cent.) and is shown to merge continuously into the formula of Ostwald with a short region of transition near  $p_1 = 0.15$ . This region is not investigated, but it is argued from the continuity and from the close equality of the values of  $a$  for different acids that single molecules of the acids do not exist in aqueous solutions of any strength, only double molecules and ions being present. Thus the study of conductivity confirms the basis of the rest of the present investigation, namely the assumption that when alcohols and fatty acids are mixed with water their molecules are double those represented by the usual chemical formulas. In the case of the acids the ions are too few to affect the other physical properties of the mixtures to an extent worth investigating without specially delicate experiments. The outcome of the whole inquiry is that the changes in most of the physical properties occurring when alcohol or fatty acid is mingled with water happen in the water through changes of its trihydrol into

dihydrol and of dihydrol into hydrol. The main difficulty encountered in the inquiry is that the physical properties of hydrol are not so nearly constant as those of ordinary substances. In connexion with solid hydrol in water of crystallization this has already been found to be the case. Hydrol dissolved in a great excess of alcohol seems to have a different density from that when it is dissolved in excess of acetic acid or that deduced for it in the liquid state from its density as a solid in water of crystallization. When hydrol is dissolved in alcohol and in acetic acid it has a different  $(n^2 - 1)/(n^2 + 2)\rho$  from that found in water of crystallization. This variation in the properties of hydrol I ascribe to the fact that the O atom in  $H_2O$  has at least one electric doublet  $\#p$  of variable moment, variable according to the electric properties of the molecules surrounding it. The properties of the hydrol molecule are more dependent on its environment than is usually the case. The view that  $H_2O\#p$  has varying properties according to the relative positions of  $\#$  and  $p$  is one that should make the investigation of hydrol of representative importance in the study of molecular and atomic architecture.

Melbourne, March 1911.

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IV. *The Emission and Absorption of Energy by Electrons.*  
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CONTENTS.

- § 1. Results and Introduction (p. 66).
- § 2. Disturbed Motion due to Radiation (p. 69).
- § 3. Significance of Wien's Law (p. 70).
- § 4. The Disturbed Orbits (p. 72).
- § 5. The Absorption of Radiation (p. 77).
- § 6. The Emission of Radiation (p. 81).
- § 7. The Complete Radiation (p. 83).

§ 1. RESULTS AND INTRODUCTION.

**L**ORENTZ'S theory of complete radiation is here extended to all wave-lengths. The negative electrons, moving in any conservative field of force due to the positive charges, absorb energy from the external radiation and by their motion return energy to it. Their velocities need not be small compared with the velocity of light; the pressure of

\* Communicated by the Author.

radiation, the Doppler effect and the change of mass are all allowed for. In the present paper, however, the negative electrons are not supposed to influence each other and the positive charges remain at rest, as in Lorentz's own work. I hope to prove elsewhere that these restrictions can be removed without altering the character of the results. Here, too, the radiation is simply assumed as an external field in addition to the other forces. I hope also to show how the radiation may be defined as distinguished from the forces of interaction of the charges, positive or negative, at any internal point of a hot body.

Let the number  $dN$  of electrons having their coordinates  $xyz$  within the volume element  $dx dy dz$ , and their momenta  $pqr$  within the triple element  $dp dq dr$ , be given by

$$dN = f(H) dp dq dr dx dy dz. \quad (1)$$

$f(H)$  is any function of  $H$ , the energy of the electron at that point of the field. Let  $E_\lambda d\lambda$  be that part of the complete radiation per unit volume for which the wave-length is between  $\lambda$  and  $\lambda + d\lambda$ . It is shown in this paper that

$$E_\lambda \int_0^\infty -\frac{d}{dH} \{\log f(H)\} \Phi(\lambda) dH = 8\pi\lambda^{-4} \int_0^\infty \Phi(\lambda) dH. \quad (2)$$

$\Phi(\lambda)$  is a function of  $\lambda$  and of  $H$  depending upon the nature of the forces.

$f(H)$  varies as  $e^{-\frac{H}{R\theta}}$  in the distribution required by the kinetic theory, and (2) reduces to

$$E_\lambda = 8\pi R\theta\lambda^{-4}, \quad (3)$$

which is Lorentz's result. If, for any cause,  $f(H)$  decreases more rapidly than  $e^{-\frac{H}{R\theta}}$ ,  $E_\lambda$  has a smaller value than (3) assigns to it.

The distribution of energy given by (3) is verified only for large values of  $\lambda\theta$ . (3) must therefore be replaced by some such formula as that of Planck :

$$E_\lambda = 8\pi ch\lambda^{-5} \left( e^{\frac{ch}{R\lambda\theta}} - 1 \right)^{-1} \quad (4)$$

(4) is not deduced from the recognized principles of dynamics. These, applied to the problem of complete radiation by the general statistical methods of Maxwell and Boltzmann, give us always (3) and nothing else. Lorentz's formula merely expresses the law of equipartition in the form it takes for radiant energy. It involves the same consequence : any configuration of a system obeying dynamical

laws, and any distribution of its motion, must be regarded as equally probable with any other in which the total energy is the same. Planck begins with the counter assertion that all distributions are not equally likely, and deduces (4) by reasoning in which ordinary dynamics is ignored.

The kinetic theory is statistical, and statistics do not necessarily throw any light on an individual case. In our actual world, energy is not, in fact, distributed as (3) would suggest. It may perhaps be maintained that though dynamical laws do not require (4), yet they may permit the distribution it represents. Hence the importance of Lorentz's method. He deals with a process of radiation and absorption almost certainly at work in metals—a process which does actually bring about for long waves the distribution of energy his formula requires. In metals there are free electrons, and Richardson's experiments even indicate that as between them the distribution of energy is approximately at least that required by the kinetic theory. I have here shown that, in so far as these electrons obey the laws of dynamics and are distributed in the manner required by the kinetic theory, they must produce equipartition of the radiant energy.

It has often been suggested that the factor  $e^{\frac{ch}{R\lambda\theta}}$  in (4) may arise somewhat thus. Radiation requires a force acting upon the electron during its collisions with the positive charges. In such a collision the force and the acceleration will reach a maximum and decrease again. For a simple example, take them proportional to  $(\alpha^2 + t^2)^{-1}$ , where  $t$  is the time. The radiation of period  $\frac{2\pi}{p}$  varies as

$$\int_{-\infty}^{+\infty} e^{ipt} (\alpha^2 + t^2)^{-1} dt \times \int_{-\infty}^{+\infty} e^{-ipt} (\alpha^2 + t^2)^{-1} dt,$$

and this, it can easily be proved, contains the factor  $e^{-2p\alpha}$ .

We need only choose such a law of force as will make  $\alpha$  a multiple of  $\theta^{-1}$ , and we have the factor required for such formulæ as (4). The result of this paper shows, however, that the absorption also contains this factor  $e^{-2p\alpha}$ , and that it disappears from the expression for the complete radiation, depending as that does only upon the ratio of emission to absorption. Whoever wishes to avoid the conclusion must, it seems to me, resign the whole system of dynamics from which it is here deduced.

## § 2. THE DISTURBED MOTION DUE TO RADIATION.

The restrictions assumed in this paper are for the most part unnecessary. It is, however, essential that we should be at liberty to treat the radiation as a small disturbing force which gradually takes the electron out of the orbit it would follow under the internal forces alone. That ensured, we can use the theory of varied motion. The displacement due to radiation must be small during the time of describing a free path—small not only by comparison with the length of the path, but also a small fraction of any wave-length dealt with.

By a free path I mean the average distance moved by the electron before the direction of its velocity is completely altered. The extent of the deviation actually produced by radiation distributed according to (4) can easily be estimated.

Let the electric intensity

$$a \cos pt + b \sin pt \quad . \quad . \quad . \quad . \quad . \quad (5)$$

act upon a particle of mass  $m$  and charge  $e$ . Then, if  $\mathbf{r}$  be the vector whose components are the coordinates of the particle

$$m \frac{d^2 \mathbf{r}}{dt^2} = e \mathbf{a} \cos pt + e \mathbf{b} \sin pt ;$$

and on integration

$$\mathbf{r} - \mathbf{r}_0 - \mathbf{t} \left( \frac{d\mathbf{r}}{dt} \right)_0 = -\frac{e\mathbf{a}}{mp^2} (\cos pt - 1) - \frac{e\mathbf{b}}{mp^2} (\sin pt - pt).$$

$\mathbf{r}_0$  and  $\left( \frac{d\mathbf{r}}{dt} \right)_0$  are the initial position and velocity, and the time  $t$  is for the free path. The left-hand side of the last equation is the deviation due to the force. Write  $\mathbf{r}_p$  for this, and denote average values by a bar :

$$\overline{\mathbf{r}_p^2} = \frac{e^2 \overline{\mathbf{a}^2}}{m^2 p^4} (\cos pt - 1)^2 + \frac{e^2 \overline{\mathbf{b}^2}}{m^2 p^4} (\sin pt - pt)^2.$$

The average value of the total energy, electric and magnetic, due to (5) is  $\frac{1}{8\pi} (\overline{\mathbf{a}^2} + \overline{\mathbf{b}^2})$  in unit volume. If that represents the energy in the interval between  $p$  and  $p + dp$ , then according to (4)

$$\frac{1}{8\pi} (\overline{\mathbf{a}^2} + \overline{\mathbf{b}^2}) = \frac{8\pi ch}{(2\pi c)^4} p^3 (e^{\frac{hp}{2\pi R\theta}} - 1)^{-1} dp ;$$

and of course  $\overline{\mathbf{a}^2} = \overline{\mathbf{b}^2}$ .

The average square of the total deviation in a given time  $t$  is the sum of such terms as  $\bar{r}_p^2$ . If we denote it by  $\bar{\delta}^2$ , then

$$\bar{\delta}^2 = \left(\frac{e}{m\pi}\right)^2 \frac{h}{c^3} \int_0^\infty \frac{du}{u} (2 - 2 \cos u - 2u \sin u + u^2)(e^{au} - 1)^{-1}, \quad (6)$$

$$u = pt \quad \text{and} \quad \alpha = h(2\pi R\theta t)^{-1}.$$

In metals, it would seem \*, the length of the free path varies inversely as the square root of the temperature, while the average velocity with which it is described varies directly in the same ratio.  $t$  is therefore inversely proportional to  $\theta$ , and  $\theta t$  is a constant.

The following numerical data are available :—

For  $\theta = 300$  the free path  $= 10^{-6}$ . Large as this seems, if we suppose the collisions to be with single atoms, it is the result obtained from the measurements of conduction in metals. Since the average velocity of the electron is  $10^7$ , it follows that  $t$  is  $10^{-13}$ . Put  $R = 10^{-16}$ ,  $h = 7 \times 10^{-27}$  (Planck), and  $\alpha$  appears to be of order unity.

$$\text{Also } \frac{e}{m} = 6 \times 10^{17}, \quad c = 3 \times 10^{10}.$$

Hence (6) reduces to

$$\bar{\delta}^2 = 10^{-23} \int_0^\infty \frac{du}{u} (2 - 2 \cos u - 2u \sin u + u^2)(e^{au} - 1)^{-1}.$$

$\bar{\delta}^2$  is of the order  $10^{-23}$ , and the mean deviation is of order  $10^{-11}$  at most, for the time of a free path.

### § 3. SIGNIFICANCE OF WIEN'S LAW.

If the time required to describe a free path is really inversely proportional to the absolute temperature, an obvious explanation of Wien's law suggests itself. Wien's formula for complete radiation in spite of minor differences agrees with Planck's in making  $E_\lambda$ , the ratio of the emission and absorption, contain a factor  $e^{-\frac{ch}{R\lambda\theta}}$  when  $\lambda\theta$  is small. We cannot without further evidence decide if this factor is to be assigned to the emission or the factor  $e^{\frac{ch}{R\lambda\theta}}$  to the absorption. Actual experiment leaves no doubt on the matter.

For by Planck's formula, the ratio of emission to absorption begins to differ from its long-wave value so soon

\* See Riecke, *Physikalische Zeitschrift*, 1909, p. 512.



as  $e^{\frac{ch}{R\lambda\theta}}$  is sensibly different from unity. For the wavelength  $4\mu$  or  $4 \times 10^{-4}$  cm. and  $\theta = 300$ ,  $\frac{ch}{R\lambda\theta}$  is about 17, and the complete radiation is infinitesimal compared with what it would be did Lorentz's formula (3) represent reality. Yet Hagen and Rubens found that for these waves there was no corresponding increase in the coefficient of absorption over that for very much larger values of  $\lambda$ . It is, therefore, the emission which decreases by containing  $e^{-\frac{ch}{R\lambda\theta}}$  as a factor. What the numerical data of last paragraph show, is that this factor is of order unity when the period of the waves is the same as the time spent by an electron on its free path. For greater wave-lengths and longer periods than this, Lorentz's formula (3) will hold; for smaller periods we shall require (4) to represent the facts by reason of the rapid decrease in the emission.

The notion of free paths and collisions is not altogether helpful when we have to do with electrons moving in a metal. If we think of the electron as completely deflected by its collision with a molecule, and remaining after that with unchanged velocity till the next collision follows, it becomes impossible to account for the actual nature of the radiation. Quite apart from all questions of dynamics as a mere matter of Fourier analysis, it is certain that the vast mass of the energy emitted would be of the same period as the time of a collision, and that is about  $10^{-15}$  of a second, taking the diameter of a molecule as  $10^{-8}$ . Up to waves of this period the emission ought to increase, not decrease, with decreasing wave-length.

The difficulty may be escaped by abandoning the notions of free path and collision in sharp contrast. The free path will be defined as the average distance an electron moves before its velocity is so changed that it retains no observable connexion with its original velocity. The length of this free path, the distance within which the original direction of motion still persists, measures the mobility of the electron. It is with that we deal in experiments on conduction. The main part of the energy emitted must be of periods not small compared with the time spent on a free path thus defined. The Fourier analysis can predict that consequence and it is independent of any dynamical theory whatever. Wien's law therefore, which makes the wave-length  $\lambda_m$  of maximum radiation vary inversely as  $\theta$ , may be interpreted as a direct consequence of the experimental fact that the time for a free path varies in the same ratio.

But to go beyond this point is to meet the great stumbling-block in the way of all theories of radiation. We may construct laws of force which make the emission a function of  $\lambda\theta$ , and so treat the problem as an exercise in the dynamics of a particle. To proceed thus is to ignore the fact that on all dynamical principles the absorption is a function of the same type as the emission and that the final conclusion is only the unwelcome paradox of equipartition.

#### § 4. THE DISTURBED ORBITS.

In what follows I treat the electron as a dynamical particle moving in a conservative field of force. The equations of motion used are Hamilton's, and the momentum may depend in any way upon the velocity or even upon the nature of the field. The vector notation is employed throughout. The problem is to find the deviation produced by the radiation.

Let  $\mathbf{r}=(x, y, z)$  denote the vector whose components are the coordinates of the electron at time  $t$ , supposing its orbit undisturbed by radiation.

$$\mathbf{u} = \frac{d\mathbf{r}}{dt},$$

$\mathbf{D}=(\xi, \eta, \zeta)$  is the displacement due to radiation.

$\mathbf{p}=(p, q, r)$  stands for the momentum of the undisturbed motion.

$\mathbf{P}=(\lambda, \mu, \nu)$  the increase of momentum due to the radiation.

Thus  $\mathbf{r} + \mathbf{D}$  and  $\mathbf{p} + \mathbf{P}$  are the position and momentum of the electron in the actual motion.

The equations of motion of the electron written in Hamilton's form are

$$\frac{d}{dt}\mathbf{p} + \nabla_{\mathbf{r}}H = 0 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{d\mathbf{r}}{dt} - \nabla_{\mathbf{p}}H = 0 \quad . \quad . \quad . \quad . \quad . \quad (8)$$

These are for the undisturbed orbit.  $\nabla_{\mathbf{r}}H$  and  $\nabla_{\mathbf{p}}H$  indicate the vectors whose components are

$$\frac{dH}{dx}, \frac{dH}{dy}, \frac{dH}{dz} \quad \text{and} \quad \frac{dH}{dp}, \frac{dH}{dq}, \frac{dH}{dr}.$$

The mass of the electron may depend in any manner whatever consistent with (7) and (8) both upon its velocity and the external field.  $H$  is the total energy.

Let  $\mathbf{E}'$  be the electric intensity on the moving electron due to the radiation. To find the deviation due to  $\mathbf{E}'$ , write

$r + D$  for  $\mathbf{r}$  and  $\mathbf{p} + \mathbf{P}$  for  $\mathbf{p}$  in (7) and (8) and expand, retaining only first powers of the displacement.

Then

$$\left. \begin{aligned} \frac{d\lambda}{dt} + \sum_{n=1}^{n=6} \frac{d^2 H}{dx d\rho_n} \sigma_n &= eE_1' \\ \frac{d\mu}{dt} + \sum_{n=1}^{n=6} \frac{d^2 H}{dy d\rho_n} \sigma_n &= eE_2' \\ \frac{d\nu}{dt} + \sum_{n=1}^{n=6} \frac{d^2 H}{dz d\rho_n} \sigma_n &= eE_3' \end{aligned} \right\} \dots \dots \dots (9)$$

$$\left. \begin{aligned} \frac{d\xi}{dt} - \sum_{n=1}^{n=6} \frac{d^2 H}{dp d\rho_n} \sigma_n &= 0 \\ \frac{d\eta}{dt} - \sum_{n=1}^{n=6} \frac{d^2 H}{dq d\rho_n} \sigma_n &= 0 \\ \frac{d\zeta}{dt} - \sum_{n=1}^{n=6} \frac{d^2 H}{dr d\rho_n} \sigma_n &= 0 \end{aligned} \right\} \dots \dots \dots (10)$$

In (9) and (10)  $\rho_n$  takes in succession the six values  $x y z p q r$  and  $\sigma_n$  the values  $\xi \eta \zeta \lambda \mu \nu$ .

$$E' \equiv (E_1', E_2', E_3').$$

(7) and (8) determine implicitly the values of  $\mathbf{r}$  and  $\mathbf{p}$  as functions of the time and of six arbitrary constants, say the initial values of the coordinates and momenta. Denote these constants, however specified, by  $\kappa_1 \kappa_2 \kappa_3 \kappa_4 \kappa_5 \kappa_6$ . Differentiate (7) and (8) with respect to any one of the  $\kappa$ 's:

$$\left. \begin{aligned} \frac{d}{dt} \left( \frac{dp}{d\kappa} \right) + \sum_{n=1}^{n=6} \frac{d^2 H}{dx d\rho_n} \frac{d\rho_n}{d\kappa} &= 0 \\ \frac{d}{dt} \left( \frac{dq}{d\kappa} \right) + \sum_{n=1}^{n=6} \frac{d^2 H}{dy d\rho_n} \frac{d\rho_n}{d\kappa} &= 0 \\ \frac{d}{dt} \left( \frac{dr}{d\kappa} \right) + \sum_{n=1}^{n=6} \frac{d^2 H}{dz d\rho_n} \frac{d\rho_n}{d\kappa} &= 0 \end{aligned} \right\} \dots \dots (11)$$

$$\left. \begin{aligned} \frac{d}{dt} \left( \frac{dx}{d\kappa} \right) - \sum_{n=1}^{n=6} \frac{d^2 H}{dp d\rho_n} \frac{d\rho_n}{d\kappa} &= 0 \\ \frac{d}{dt} \left( \frac{dy}{d\kappa} \right) - \sum_{n=1}^{n=6} \frac{d^2 H}{dq d\rho_n} \frac{d\rho_n}{d\kappa} &= 0 \\ \frac{d}{dt} \left( \frac{dz}{d\kappa} \right) - \sum_{n=1}^{n=6} \frac{d^2 H}{dr d\rho_n} \frac{d\rho_n}{d\kappa} &= 0 \end{aligned} \right\} \dots \dots \dots (12)$$

There are altogether six sets of equations such as (11) and (12), where  $\kappa$  takes in succession six different values.

Multiply the first of the group (9) by  $\frac{dx}{d\kappa}$  and the first of (11) by  $\xi$  and subtract :

$$\frac{d\lambda}{dt} \frac{dx}{d\kappa} - \xi \frac{d}{dt} \left( \frac{dp}{d\kappa} \right) + \sum_{n=1}^{n=6} \frac{d^2 H}{dx d\rho_n} \left( \sigma_n \frac{dx}{d\kappa} - \xi \frac{d\rho_n}{d\kappa} \right) = eE_1' \frac{dx}{d\kappa}. \quad (13)$$

Similarly from the first equations in (10) and (12)

$$\frac{d\xi}{dt} \frac{dp}{d\kappa} - \lambda \frac{d}{dt} \left( \frac{dx}{d\kappa} \right) - \sum_{n=1}^{n=6} \frac{d^2 H}{dp d\rho_n} \left( \sigma_n \frac{dp}{d\kappa} - \lambda \frac{d\rho_n}{d\kappa} \right) = 0. \quad (14)$$

There are altogether three equations, of which (13) is the first, and three represented by (14). Add together the first three and subtract them from the sum of the three others. Then it can easily be shown that the terms involving  $H$  all vanish, a well-known result in the theory of varied motion. And

$$\frac{d}{d\kappa} \left( D \frac{dp}{d\kappa} - P \frac{dx}{d\kappa} \right) = -eE' \frac{dx}{d\kappa}, \quad . \quad . \quad . \quad (15)$$

(15) represents six equations got by taking the six particular values for  $\kappa$ . On integration

$$D \frac{d}{d\kappa} p - P \frac{d}{d\kappa} x = -e \int_{t_0}^t E' \frac{dx}{d\kappa}. \quad . \quad . \quad . \quad (16)$$

The question arises how  $t_0$ , the lower limit of integration in (16), is to be determined.

The deviation of an electron from the orbit it would describe were there no disturbing force is continuous. In order, however, to find the absorption produced, it is necessary to take a section across this indivisible process. I shall deal with the absorption between the times  $t_b$  and  $t_a$ . Take the lower limit  $t_0$  in (16) such that  $t_b - t_0$  is at least of the order of the time in a free path. The deviation as given by (16) is then reckoned zero at  $t_0$ , and between the time  $t_b$  and  $t_a$  it is due wholly to the radiation which has acted from the time  $t_0$ . Also the position and momentum in the undisturbed orbit between  $t_b$  and  $t_a$  bears no relation to the forces of radiation which have produced the deviation. For this orbit is the prolongation of that which the particle began

to trace at  $t_0$ , and from  $t_0$  to  $t_b$  it has been completely dominated by the internal forces of the field.

On solving the six equations for which (16) stands,

$$D = - \sum_{n=1}^{n=6} \frac{M_n}{\Delta} \int_{t_0}^t eE' \frac{dr}{d\kappa_n} dt. \quad (17)$$

$$P = \sum_{n=1}^{n=6} \frac{M'_n}{\Delta} \int_{t_0}^t eE' \frac{dr}{d\kappa_n} dt. \quad (18)$$

$$\Delta = \begin{vmatrix} \frac{dp}{d\kappa_1} & \frac{dq}{d\kappa_1} & \frac{dr}{d\kappa_1} & \frac{dx}{d\kappa_1} & \frac{dy}{d\kappa_1} & \frac{dz}{d\kappa_1} \\ \frac{dp}{d\kappa_2} & . & . & . & . & . \\ \frac{dp}{d\kappa_3} & . & . & . & . & . \\ \frac{dp}{d\kappa_4} & . & . & . & . & . \\ \frac{dp}{d\kappa_5} & . & . & . & . & . \\ \frac{dp}{d\kappa_6} & . & . & . & . & . \end{vmatrix}. \quad (19)$$

$$M_n = (M_{1n}, M_{2n}, M_{3n}). \quad (20)$$

$$M'_n = (M_{4n}, M_{5n}, M_{6n}). \quad (21)$$

Here  $M_{1n}$  is the minor of the first column and  $n$ th row in  $\Delta$ , and the other symbols in (20) and (21) have like meanings. It is well known that  $\Delta$  is a constant independent of the time, and if the constants  $\kappa$  are the positions and momenta at any one time  $\Delta=1$ .

The radiation is defined by the electromagnetic equations:

$$\frac{1}{c} \frac{dE}{dt} = \text{Curl } H. \quad (22)$$

$$\frac{1}{c} \frac{dH}{dt} = -\text{Curl } E. \quad (23)$$

$$E' = E + \frac{1}{c} [uH]. \quad (24)$$

E may be supposed given by a series of terms of the simple harmonic type. Taking one of these,

$$E = l_1 \{ (\alpha + i\beta) e^{ipt_1} + (\alpha - i\beta) e^{-ipt_1} \}. \quad (25)$$

$$t_1 = t - l_1 r/c, \quad (26)$$

where  $\alpha + i\beta$  and  $\alpha - i\beta$  are conjugates, and

$$l = (l, m, n), \quad l_1 = (l_1, m_1, n_1), \quad ll_1 = 0, \quad (27)$$

(25) represents a wave travelling parallel to the lines whose direction cosines are  $l, m, n$ , the components of  $l$ , and polarized in the perpendicular direction  $l_1$ .

From (25) and (23)

$$H = [ll_1] \{ (\alpha + i\beta) e^{ipt_1} + (\alpha - i\beta) e^{-ipt_1} \};$$

$$E' = \left\{ l_1 + \left[ \frac{1}{c} \frac{dr}{dt} [ll_1] \right] \right\} (\alpha + i\beta) e^{ipt_1} + \text{Conjugate};$$

$$E' = \left\{ \left( 1 - l \frac{dr}{cdt} \right) l_1 + \left( l_1 \frac{dr}{cdt} \right) l \right\} (\alpha + i\beta) e^{ipt_1} + \text{Conj.};$$

and

$$E' \frac{dr}{d\kappa_n} = \left\{ \left( 1 - l \frac{dr}{cdt} \right) l_1 \frac{dr}{d\kappa_n} + l_1 \frac{dr}{cdt} l \frac{dr}{d\kappa_n} \right\} (\alpha + i\beta) e^{ipt_1} + \text{Conj.};$$

or

$$E' \frac{dr}{d\kappa_n} = \frac{\alpha + i\beta}{ip} \frac{d}{dt} \left( l_1 \frac{dr}{d\kappa_n} e^{ipt_1} \right) - \frac{\alpha + i\beta}{ip} \frac{d}{d\kappa_n} \left( l_1 \frac{dr}{dt} e^{ipt_1} \right) + \text{Conj.} \quad (28)$$

Using (28) in (17) and (18)

$$D = -e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M_n \left\{ l_1 \frac{dr}{d\kappa_n} e^{ipt_1} \right\}_t^t + e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M_n \frac{k}{d\kappa_n} \left\{ \int_{t_0}^t l_1 \frac{dr}{dt} e^{ipt_1} dt \right\} + \text{Conj.} \quad (29)$$

$$P = e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M'_n \left\{ l_1 \frac{dr}{d\kappa_n} e^{ipt_1} \right\}_{t_0}^t - e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M'_n \frac{d}{d\kappa_n} \left\{ \int_{t_0}^t l_1 \frac{dr}{dt} e^{ipt_1} dt \right\} + \text{Conj.} \quad (30)$$

The first terms in (29) and (30) result from an integration between the limits  $t_0$  and  $t$ , and the values at the lower limit must be subtracted from those at the upper. The complete

expressions for D and P require the terms conjugate to those written. Remembering (19), (20), and (21),

$$D = e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M_n \left( 1_1 \frac{dr}{d\kappa_n} e^{ipt_1} \right)_0 + e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M_n \frac{d}{d\kappa_n} \left\{ \int_{t_0}^t 1_1 \frac{dr}{dt} e^{ipt_1} dt \right\} + \text{Conj.} \quad (31)$$

$$P = -e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M_n' \left( 1_1 \frac{dr}{d\kappa_n} e^{ipt_1} \right)_0 + e \frac{(\alpha + i\beta)}{ip} 1_1 e^{ipt_1} - e \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} M_n' \frac{d}{d\kappa_n} \left\{ \int_{t_0}^t 1_1 \frac{dr}{dt} e^{ipt_1} dt \right\} + \text{Conj.} \quad (32)$$

Where  $\left( 1_1 \frac{dr}{d\kappa_n} e^{ipt_1} \right)_0$  denotes the value at  $t_0$ .

## § 5. THE ABSORPTION OF RADIATION.

The rate of absorption of energy is the electric force multiplied by the velocity. In the undisturbed motion this is

$$eE \frac{dr}{dt} \quad \text{or} \quad eE \nabla_p H,$$

and, on the average, it is zero between  $t_b$  and  $t_a$ , because only by the deviation produced is energy absorbed. Write

$$\phi = E \nabla_p H. \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$\phi$  is therefore expressed as a function of the time momenta and position, the time entering explicitly through E. If in the disturbed motion  $\phi$  becomes  $\phi + \delta\phi$ , the total absorption between  $t_b$  and  $t_a$  is

$$e \int_{t_b}^{t_a} \delta\phi dt = e \int_{t_b}^{t_a} D \nabla_r \phi dt + e \int_{t_b}^{t_a} P \nabla_p \phi dt, \quad . \quad (34)$$

and in (34) the values of D and P given by (31) and (32) are to be used.

It is plain that only terms which contain the product of the conjugates  $\alpha + i\beta$  and  $\alpha - i\beta$  will contribute to (34). The first terms in (31) and (32), those which involve  $t_0$ , will yield nothing, for the time  $t_0$  antedates  $t_b$  by at least the length of a free path. Even if we are considering light waves whose period is long compared with the time  $t_b - t_0$ , our definition of free path requires that there should be no correlation between the factors  $M_n$  and  $\left( \frac{dr}{d\kappa_n} \right)_0$ . For

waves of period greater than this the product  $e^{ip(t_1-t_0)}$  is accidental in sign. The second term on the right of (32) and its conjugate also contribute nothing to (34). They give

$$\begin{aligned} & e^2 \frac{(\alpha^2 + \beta^2)}{ip} \mathbf{l}_1 e^{ipt_1} \nabla_{\mathbf{p}} (\mathbf{l}_1 e^{-ipt_1} \nabla_{\mathbf{p}} H) + \text{Conj.} \\ & = e^2 \frac{(\alpha^2 + \beta^2)}{ip} \mathbf{l}_1 \nabla_{\mathbf{p}} (\mathbf{l}_1 \nabla_{\mathbf{p}} H) + \text{Conj.}, \end{aligned}$$

since  $t_1$  does not contain  $\mathbf{p}$ . This last expression consists of two conjugate imaginaries and reduces to zero. The whole absorption therefore is derived from the last set of terms in (31) and (32). It is at the rate

$$e^2 \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} (\nabla_{\mathbf{r}} \phi \cdot \mathbf{M}_n - \nabla_{\mathbf{p}} \phi \cdot \mathbf{M}_n') \frac{d}{d\kappa_n} \left\{ \int_{t_0}^t \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt \right\} + \text{Conj.} \quad (35)$$

It is easily verified from the form of  $\Delta$  that

$$\sum_{n=1}^{n=6} \frac{d}{d\kappa_n} \mathbf{M}_n = 0 \quad \text{and} \quad \sum_{n=1}^{n=6} \frac{d}{d\kappa_n} \mathbf{M}_n' = 0,$$

(35) becomes

$$\begin{aligned} & e^2 \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} \nabla_{\mathbf{r}} \phi \frac{d}{d\kappa_n} \left( \mathbf{M}_n \int_{t_0}^t \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt \right) \\ & - e^2 \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} \nabla_{\mathbf{p}} \phi \frac{d}{d\kappa_n} \left( \mathbf{M}_n' \int_{t_0}^{t_1} \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt \right) + \text{Conj.} \quad (36) \end{aligned}$$

Now, whatever function  $\psi$  may be of the coordinates and momenta,

$$\begin{aligned} \frac{d\psi}{d\kappa_n} &= \sum_{n=1}^{n=6} \frac{d\psi}{dx} \frac{dx}{d\kappa_n} + \frac{d\psi}{dy} \frac{dy}{d\kappa_n} + \frac{d\psi}{dz} \frac{dz}{d\kappa_n} \\ &+ \frac{d\psi}{dp} \frac{dp}{d\kappa_n} + \frac{d\psi}{dq} \frac{dq}{d\kappa_n} + \frac{d\psi}{dr} \frac{dr}{d\kappa_n}. \end{aligned}$$

And on solving these equations

$$\nabla_{\mathbf{r}} \psi = \sum_{n=1}^{n=6} \mathbf{M}_n' \frac{d\psi}{d\kappa_n} \quad . \quad . \quad . \quad . \quad (37)$$

$$\nabla_{\mathbf{p}} \psi = \sum_{n=1}^{n=6} \mathbf{M}_n \frac{d\psi}{d\kappa_n} \quad . \quad . \quad . \quad . \quad (38)$$

(36) can be written

$$\begin{aligned} & e^2 \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} \frac{d}{d\kappa_n} \left\{ (\nabla_{\mathbf{r}} \phi \cdot \mathbf{M}_n - \nabla_{\mathbf{p}} \phi \cdot \mathbf{M}_n') \times \int_{t_0}^t \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt \right\} \\ & - e^2 \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} \left\{ \mathbf{M}_n \frac{d}{d\kappa_n} (\nabla_{\mathbf{r}} \phi) - \mathbf{M}_n' \frac{d}{d\kappa_n} (\nabla_{\mathbf{p}} \phi) \right\} \times \int_{t_0}^t \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt. \quad (39) \end{aligned}$$



Now

$$\sum_{n=1}^{n=6} M_n' \frac{d}{d\kappa_n} (\nabla_{\mathbf{p}} \phi) = \frac{d^2 \phi}{dx dp} + \frac{d^2 \phi}{dy dq} + \frac{d^2 \phi}{dz dr} \text{ by (37).}$$

And

$$\sum_{n=1}^{n=6} M_n \frac{d}{d\kappa_n} (\nabla_{\mathbf{r}} \phi) = \frac{d^2 \phi}{dp dx} + \frac{d^2 \phi}{dq dy} + \frac{d^2 \phi}{dr dz} \text{ by (38).}$$

Thus the expression (39) reduces to its first term only and the absorption between the time  $t_b$  and  $t_a$  is

$$e^2 \frac{(\alpha + i\beta)}{\Delta ip} \sum_{n=1}^{n=6} \frac{d}{d\kappa_n} \left\{ \int_{t_b}^{t_a} (M_n \cdot \nabla_{\mathbf{r}} \phi - M_n' \cdot \nabla_{\mathbf{p}} \phi) \psi_{(ip)} dt \right\} + \text{Conjugate, (40)}$$

where

$$\psi_{(ip)} = \int_{t_0}^t \mathbf{1} \frac{d\mathbf{r}}{dt} e^{ipt_1} dt.$$

This cannot be reduced further without assuming a certain average distribution of the electrons. I take now for the six constants  $\kappa$  the coordinates and momenta in an undisturbed orbit. Since the radiation causes only an infinitesimal deviation, the distribution is that brought about by the internal forces. Choosing the  $\kappa$ 's thus  $\Delta = 1$ , and I shall suppose that the number  $dN$  in the sextuple element is

$$dN = f(H_b) d\kappa_1 d\kappa_2 d\kappa_3 d\kappa_4 d\kappa_5 d\kappa_6.$$

Then the absorption between  $t_a$  and  $t_b$  is for all the electrons

$$e^2 \frac{(\alpha + i\beta)}{ip} \iiint \sum_{n=1}^{n=6} \frac{d}{d\kappa_n} \left\{ \int_{t_b}^{t_a} (\nabla_{\mathbf{r}} \phi \cdot M_n - \nabla_{\mathbf{p}} \phi \cdot M_n') \psi_{(ip)} dt \right\} dN + \text{Conj. (41)}$$

Through the undisturbed orbit the total energy is constant,

$$H = H_b.$$

And as in (37) and (38)

$$\nabla_{\mathbf{r}} H = \sum_{n=1}^{n=6} M_n' \frac{dH_b}{d\kappa_n};$$

$$\nabla_{\mathbf{p}} H = \sum_{n=1}^{n=6} M_n \frac{dH_b}{d\kappa_n}.$$

If we integrate (41) by parts, remembering the value of

$dN$  above and using these last results, it becomes

$$e^2 \frac{(\alpha + i\beta)}{ip} \iiint \sum_{n=1}^{n=6} \frac{d}{d\kappa_n} \left\{ \int_{t_b}^{t_a} [f(H) \cdot \nabla_r \phi \cdot M_n - f(H) \nabla_p \phi M_n'] \psi_{ip} dt \right\} dv_b dV_b + \text{Conj.}$$

$$- e^2 \frac{(\alpha + i\beta)}{ip} \iiint \int_{t_b}^{t_a} f'(H) \{ \nabla_p H \cdot \nabla_r \phi - \nabla_r H \cdot \nabla_p \phi \} \psi_{ip} dt dv_b dV_b + \text{Conj.} \quad (42)$$

$$dv_b = d\kappa_1 d\kappa_2 d\kappa_3, \quad dV_b = d\kappa_4 d\kappa_5 d\kappa_6.$$

Also  $dv dV = dv_b dV_b$ ;

$\kappa_1, \kappa_2, \kappa_3$  are the coordinates at  $t_b$ ;

and  $\kappa_4, \kappa_5, \kappa_6$  are the momenta.

If the equations of dynamics hold everywhere, then these coordinates of position and the momenta are extended at any time all over the radiating body. The first set of terms in (42), being perfect differentials, vanish.

In the second term of (42)

$$\nabla_p H \cdot \nabla_r \phi - \nabla_r H \cdot \nabla_p \phi = \nabla_r \phi \cdot \frac{d\mathbf{r}}{dt} + \nabla_p \phi \frac{d\mathbf{p}}{dt} \text{ from (7) \& (8).}$$

$$= \frac{\partial \phi}{\partial t} - \frac{d\phi}{dt},$$

where  $\frac{\partial \phi}{\partial t}$  is the total differential of  $\phi$  with respect to  $t$ , and  $\frac{d\phi}{dt}$  is the explicit differential.

$$\frac{\partial \phi}{\partial t} - \frac{d\phi}{dt} = (\alpha + i\beta) e^{ipt} \frac{d}{dt} \left( \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{-ip\mathbf{r}/c} \right) + \text{Conj. by (25) and (33).}$$

And inserting this in (42) it reduces to

$$- e^2 \frac{(\alpha^2 + \beta^2)}{ip} \iiint \int_{t_b}^{t_a} f'(H) e^{-ipt} \frac{d}{dt} \left( \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{ip\mathbf{r}/c} \right) \psi_{(ip)} dt dv dV + \text{Conj.} \quad \dots \quad (43)$$

On integration by parts (43) becomes

$$- e^2 \frac{(\alpha^2 + \beta^2)}{ip} \iiint f'(H) \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{-ipt_1} \int_{t_0}^{t_a} \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt dv dV ;$$

$$+ e^2 \frac{(\alpha^2 + \beta^2)}{ip} \iiint f'(H) \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{-ipt_b} \int_{t_0}^{t_b} \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{ipt_b} dt dv dV ;$$

$$- e^2 (\alpha^2 + \beta^2) \iiint f'(H) \int_{t_b}^{t_a} \mathbf{1}_1 \frac{d\mathbf{r}}{dt} e^{-ipt} \psi_{(ip)} dt dv dV + \text{Conjugates.} \quad (44)$$

The average value of the first two terms in (44) is zero, but in any case in a steady state they will cancel, since  $t_0$  is taken so far back that all the terms in the integral

$$\int_{t_0}^{t_b} \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt,$$

which are correlated with  $\frac{d\mathbf{r}}{dt_b} e^{-ipt_1b}$  are included.

Thus the absorption between  $t_b$  and  $t_a$  reduces to

$$-e^2(\alpha^2 + \beta^2) \iiint \iiint f'(H) \int_{t_b}^{t_a} \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{-ipt_1} \psi_{(ip)} dt dv dV. \quad (45)$$

Or if we integrate for all orbits in which the energy is between  $H$  and  $H + dH$ , the absorption can be expressed as

$$-e^2(\alpha^2 + \beta^2) \int_0^\infty \frac{f'(H)}{j(H)} \Phi(\lambda) dH, \quad \dots \quad (46)$$

or, if we suppose  $f(H)$  to vary as  $e^{-\frac{H}{R\theta}}$ ,

$$e^2 \frac{(\alpha^2 + \beta^2)}{R\theta} \int_0^\infty \Phi(\lambda) dH, \quad \dots \quad (47)$$

$\Phi(\lambda)$  being a function of  $H$ , and the wave-length  $\lambda$ .

## § 6. THE EMISSION OF RADIATION.

Turn now to the question of emission. Take a point in the direction  $\mathbf{l}$  from the origin and at the distance  $R$ , which is very great compared with the distance  $r$  of the electron. The vector and scalar potential at this point at the time  $t'$  are given by

$$\mathbf{F} = \frac{e}{cR} \frac{d\mathbf{r}}{dt} \left( 1 - \mathbf{l} \frac{d\mathbf{r}}{cdt} \right)^{-1} \quad \dots \quad (48)$$

$$\phi = \frac{e}{R} \left( 1 - \mathbf{l} \frac{d\mathbf{r}}{cdt} \right)^{-1} \quad \dots \quad (49)$$

See for (48) and (49) (Bucherer, *Einführung in der Elektronen Theorie*)

$$t' = t - \mathbf{l} \frac{\mathbf{r}}{c} + \frac{R}{c} = t_1 + \frac{R}{c}.$$

In (48) and (49) only the first power of  $R^{-1}$  is retained. The electric and magnetic intensities are given by

$$\mathbf{E} = -\frac{1}{c} \frac{d\mathbf{F}}{dt} - \nabla\phi. \quad \mathbf{H} = \text{Curl } \mathbf{F}.$$

Then the flux of energy per unit time across unit area is

$$\frac{c}{4\pi} [\mathbf{E}\mathbf{H}].$$

The energy of waves polarized in the direction  $\mathbf{l}_1$  which cross an element  $dS$  of area on the sphere of radius  $R$  is

$$\frac{1}{4\pi} \frac{d}{dt'} (\mathbf{l}_1 \mathbf{F}) \times \frac{d}{dR} (\mathbf{l}_1 \mathbf{F}) dS. \quad . \quad . \quad . \quad (50)$$

In the first factor of (50)  $\nabla\phi$  is omitted, since it is of order  $R^{-2}$ .

$$\text{Also} \quad \frac{d}{dR} (\mathbf{l}_1 \mathbf{F}) = \frac{1}{c} \frac{d}{dt'} (\mathbf{l}_1 \mathbf{F}).$$

The energy of period  $\frac{2\pi}{p}$  involved in (50) is found by the Fourier analysis. There is emitted in any interval of time  $T$  the amount

$$\frac{dS}{4\pi^2 c} \frac{dp}{c} \int_0^T \frac{d}{dt'} (\mathbf{l}_1 \mathbf{F}) e^{-ipt'} dt' \times \int_0^T \frac{d}{dt'} (\mathbf{l}_1 \mathbf{F}) e^{ipt'} dt'.$$

On integration by parts this becomes

$$\frac{dS}{4\pi^2 c} \frac{p^2 dp}{c} \int_0^T \mathbf{l}_1 \mathbf{F} e^{-ipt'} \frac{dt'}{dt} dt \times \int_0^T \mathbf{l}_1 \mathbf{F} e^{ipt'} \frac{dt'}{dt} dt,$$

or

$$\frac{dS}{R^2} \frac{p^2 dp e^2}{4\pi^2 c^3} \int_0^T \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{-ipt_1} dt \times \int_0^T \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{ipt_1} dt,$$

or

$$\frac{dS}{R^2} \frac{e^2 p^2 dp}{4\pi^2 c^3} \int_0^T \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{-ipt_1} \psi_{(ip)} dt + \text{Conjugate}.$$

And between the times  $t_b$  and  $t_a$  on the average the amount of emission is

$$\frac{dS}{R^2} \frac{e^2 p^2 dp}{4\pi^2 c^3} \int_{t_b}^{t_a} \mathbf{l}_1 \frac{d\mathbf{r}}{dt} e^{-ipt_1} \psi_{(ip)} dt + \text{Conjugate}. \quad . \quad (51)$$

This is the part of the emitted energy which travels within the solid angle  $\frac{dS}{R^2}$  in the direction  $\mathbf{l}$  and is polarized along  $\mathbf{l}_1$ .

$$\text{Put } \frac{dS}{R^2} = d\Omega.$$

The total emission for all electrons is found by integration of (51), it is

$$d\Omega \frac{e^2 p^2 dp}{4\pi^2 c^3} \iiint f(H) \int_{t_b}^{t_a} \mathbf{l}_1 \frac{dr}{dt} e^{-ipt_1} \psi_{(ip)} dt dv dV + \text{Conj.},$$

or using the same notation as in (46) or (47)

$$d\Omega \frac{e^2 p^2 dp}{4\pi^2 c^3} \int_0^\infty \Phi(\lambda) dH. \quad (52)$$

## § 7. THE COMPLETE RADIATION.

In complete radiation there must be equality in the emission and absorption of energy in any direction. Where (47) represents the emission (52) shows that

$$\alpha^2 + \beta^2 = R\theta \frac{p^2 dp}{4\pi^2 c^3} d\Omega. \quad (53)$$

The total energy per unit volume in the wave train (25) is,

$$\frac{1}{2\pi} (\alpha^2 + \beta^2).$$

And the whole energy per unit volume in the interval  $dp$  is, according to (53),

$$\frac{1}{\pi} \int R\theta \frac{p^2 dp}{4\pi^2 c^3} d\Omega \quad \text{or} \quad R\theta \frac{p^2 dp}{\pi^2 c^3},$$

allowing for two waves polarized at right angles and both travelling along  $\mathbf{l}$ .

Since  $\lambda = \frac{2\pi c}{p}$  this gives Lorentz's result

$$E_\lambda = 8\pi R\theta \lambda^{-4}.$$

If (46) gives the absorption instead of (47) we have no longer (53), and instead of Lorentz's formula

$$E_\lambda \int_0^\infty -\frac{d}{dH} \{\log f(H)\} \Phi(\lambda) dH = 8\pi \lambda^{-4} \int_0^\infty \Phi(\lambda) dH.$$

V. *The Relation of Temperature and Molecular Attraction.*  
By J. E. MILLS\*.

PART I.—*The Law of Molecular Attraction.*

IN a series of papers† in the Philosophical Magazine Dr. R. D. Kleeman has investigated a possible *fifth power law* of the molecular attraction, and in this investigation he has used data taken from a paper by the author. Dr. Kleeman seems entirely to have overlooked the fact that the data were used by the author to prove the truth of an equation of the form

$$\frac{L - E_e}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant, or } \lambda = \mu' (\sqrt[3]{d} - \sqrt[3]{D}). \quad (1)$$

Here  $L$  is the heat of vaporization of one gram of the liquid,  $E_e$  is the energy spent in overcoming the external pressure as the liquid expands to the volume of the saturated vapour.  $L - E_e$  is therefore the so-called internal heat of vaporization, and is called  $\lambda$ .  $d$  and  $D$  are the densities of the liquid and saturated vapour respectively at the temperature of the vaporization. The constant given by the equation is called  $\mu'$ .

This relation was theoretically derived on the supposition that the molecular attraction varied inversely as the square of the distance apart of the molecules, that it did not vary with the temperature, and that the total force proceeding from a molecule was a constant for any particular molecule. The equation has been extensively studied and discussed by the author‡, and it is certain that if the equation is true many of the conclusions of Kleeman are erroneous.

There is no doubt whatever that the equation is true. The fact that the proof has been so completely overlooked by Kleeman is a sufficient reason for republishing here a very brief summary of the results obtained for comparison with his results. I give such a summary in Table I. below. A mean value of the constant rather arbitrarily chosen for each

\* Communicated by the Author.

† Phil. Mag. xix. p. 795 (1910), and later articles.

‡ Journ. Phys. Chem. vi. p. 209 (1902); viii. p. 383 (1904); viii. p. 593 (1904); ix. p. 402 (1905); x. p. 1 (1906); xi. p. 132 (1907); xi. p. 594 (1907); xiii. p. 512 (1909); Journ. Amer. Chem. Soc. xxvi. p. 1099 (1909); Phil. Mag. Oct. 1910; Journ. Phys. Chem. May 1911. These papers need revision badly. The eighth paper should be read first, then the last two papers mentioned. The remaining papers can then be briefly examined in the order in which they were written, making allowance for some necessary changes. See also Mills and MacRae, Journ. Amer. Chem. Soc. xxxii. p. 1162 (1910).

TABLE I.

Mean $\mu'$ .....	Ethyl oxide 103.8.	Di-iso- propyl 96.48.	Di-iso- butyl 87.72.	Isopen- tane 105.5.	Normal pentane 110.0.	Normal hexane 102.80.
Temperature 0° C.	+ 105.6	97.8	+ 89.1	+ 107.2	+ 111.1	103.6
10	+ 104.8	—	—	104.5	—	—
20	103.9	—	—	105.1	—	—
30	103.4	—	—	105.1	108.6	—
40	103.0	—	—	104.8	109.4	—
50	102.9	97.9	—	104.7	109.3	—
60	102.9	97.9	—	104.5	109.6	102.4
70	102.7	98.0	—	104.4	109.7	102.7
80	102.9	98.1	—	105.0	109.8	103.0
90	103.2	97.8	87.9	105.4	109.9	103.0
100	103.6	97.6	87.4	105.9	110.0	103.1
110	103.8	97.5	86.8	106.0	110.5	103.4
120	104.1	97.6	86.0	106.3	+ 111.1	103.5
130	104.6	97.5	86.0	106.5	111.0	103.4
140	+ 105.0	97.5	— * 84.9	+ 106.7	110.5	103.0
150	+ 105.1	97.5	— * 84.7	+ 106.9	110.5	103.1
160	104.6	97.7	— * 85.0	+ 106.7	110.3	102.5
170	103.5	97.7	— * 85.6	105.5	110.3	102.4
180	101.9	98.0	86.2	103.4	109.3	102.6
190	— *	98.1	86.8	—	— *	102.8
200	—	98.1	87.0	—	—	102.7
210	—	97.3	87.3	—	—	102.1
220	—	94.8	87.9	—	—	101.1
230	—	—	+ 88.6	—	—	— *
240	—	—	+ 89.0	—	—	—
250	—	—	+ 89.5	—	—	—
260	—	—	+ 89.4	—	—	—
270	—	—	87.6	—	—	—
280	—	—	—	—	—	—
Critical tem- perature .....	193° 8	227° 35	276° 8	187° 8	197° 2	234° 8
Average $\mu'$ .....	103.76	97.53	87.58	105.46	109.94	102.80
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	102.0	96.5	80.7	107.0	109.4	99.2

TABLE I. (*continued*).

Mean $\mu'$ .....	Normal heptane 98.2.	Normal octane 92.78.	Hexa- methylene 103.63.	Benzene 109.23	Fluor- benzene 85.65.	Chlor- benzene 81.42.
Temperature						
0° C.	99.6	+ *	102.6	108.3	85.0	+ *
10	—	97.5	—	—	—	—
20	—	—	—	—	—	—
30	—	—	—	—	—	—
40	—	—	—	—	—	—
50	—	—	—	—	—	—
60	—	—	—	—	—	—
70	98.7	—	—	108.7	—	—
80	99.3	—	104.3	109.2	+ 86.8	—
90	99.2	—	104.3	109.1	+ 86.8	—
100	98.9	—	104.1	108.7	+ 86.9	—
110	98.6	—	103.9	108.3	86.4	—
120	98.2	92.6	103.4	107.6	86.1	—
130	97.7	92.9	103.0	107.9	85.8	79.9
140	97.4	92.7	102.9	108.2	85.3	80.3
150	97.2	92.5	102.5	108.5	84.9	80.7
160	97.4	92.7	102.8	109.1	84.7	80.9
170	97.7	92.4	102.7	109.4	84.8	81.1
180	98.5	92.7	103.4	110.1	84.9	81.5
190	98.9	92.8	102.9	110.1	84.8	81.5
200	99.2	93.0	103.1	110.1	84.9	81.6
210	+ 99.7	93.9	103.5	+ 110.7	85.3	81.7
220	+ 99.7	93.6	104.2	+ 110.5	85.7	82.2
230	+ 99.8	93.9	104.6	+ 110.4	85.9	82.4
240	+ 99.8	93.7	104.6	+ 110.4	86.3	+ 82.8
250	99.3	+ 94.2	+ 104.9	+ 110.5	+ 86.6	+ 82.9
260	96.6	+ 94.6	104.7	110.2	+ 86.6	+ 82.7
270	—	+ 94.3	103.4	109.3	85.8	82.5
280	—	93.4	—	107.8	84.0	—
290	—	91.0	—	—	—	—
Critical tem- perature .....	266° 90	296° 0.2	280° 0	288° 0.5	286° 55	359° 1
Average $\mu'$ .....	98.64	93.16	103.63	109.26	85.65	81.66
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	90.8	84.2	104.5	110.5	85.2	81.3



TABLE I. (continued).

Mean $\mu'$ .....	Bromo- benzene 55·37.	Iodo- benzene 43·46.	Carbon tetra- chloride 44·29.	Stannic chloride 26·51.	Methyl formate 119·86.	Ethyl formate 107·14.
Temperature						
0° C.	—	—	43·5	26·2	+ * 123·9	+ 108·8
10	—	—	—	—	—	—
20	—	—	—	—	—	—
30	+ * 57·6	+ 44·2	—	—	+ 122·1	—
40	—	—	—	—	+ 121·4	—
50	—	—	—	—	121·0	+ 108·5
60	—	—	—	—	120·3	+ 108·4
70	—	—	43·5	—	119·6	108·2
80	—	—	43·5	—	119·4	107·8
90	—	—	43·6	—	119·4	107·5
100	—	—	43·5	26·7	119·1	107·4
110	—	—	43·5	26·7	119·7	107·3
120	—	—	43·5	26·7	120·1	107·1
130	—	—	43·4	26·7	119·8	106·9
140	—	—	43·5	26·5	119·8	106·9
150	54·6	—	43·5	26·5	119·7	106·5
160	54·6	—	43·8	26·5	119·2	106·5
170	54·8	—	44·0	26·5	119·1	106·0
180	55·0	42·7	43·9	26·5	118·1	106·4
190	55·2	42·9	44·0	26·4	— * 116·4	— 106·0
200	55·4	43·1	44·2	26·3	— * 113·3	— 105·1
210	55·7	43·3	44·3	26·4	— * 106·6	— * 103·8
220	55·9	43·5	+ 44·5	26·4	—	— * 101·3
230	56·0	43·6	+ 44·8	26·5	—	— * 97·6
240	55·8	43·6	+ 44·9	26·5	—	—
250	55·8	43·6	+ 45·2	26·5	—	—
260	+ 56·1	43·4	+ 45·0	26·5	—	—
270	+ 56·2	43·2	+ 44·5	26·4	—	—
280	—	—	43·9	26·4	—	—
Critical tem- perature .....	397°	448°	283°·15	318°·7	214°·0	235°·3
Average $\mu'$ .....	55·47	43·37	44·01	26·51	119·86	107·14
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	56·3	43·8	45·3	25·9	119·8	103·9

TABLE I. (*continued*).

Mean $\mu'$ .....	Methyl acetate 108.8.	Propyl formate 98.79.	Ethyl acetate 98.0.	Methyl propionate 99.02.	Propyl acetate 92.30.
Temperature		+	+	—	+
0° C.	110.7	100.8	102.2	97.8	97.1
10	—	—	—	—	—
20	—	—	—	—	—
30	—	—	—	—	—
40	—	—	—	—	—
50	110.3	—	—	—	—
60	110.7	—	—	—	—
70	110.6	+ 100.0	99.3	99.9	—
80	110.5	+ 100.3	99.6	99.8	—
90	109.9	99.5	99.8	99.8	94.0
100	109.7	99.1	99.9	99.3	93.8
110	109.6	98.8	99.9	99.2	94.0
120	109.6	98.5	99.7	99.1	93.9
130	109.6	98.4	99.2	99.1	93.5
140	109.7	98.5	99.2	98.9	93.2
150	109.9	98.0	98.6	98.9	93.2
160	109.8	97.8	98.2	98.9	93.3
170	109.5	— 97.6	98.6	98.6	93.0
180	108.8	97.8	98.6	98.8	93.2
190	108.5	98.5	98.7	99.1	93.2
200	108.2	98.5	98.9	99.5	93.2
210	107.0	98.4	98.7	99.4	93.3
220	— <sup>*</sup> 105.0	99.2	97.7	99.4	93.2
230	— <sup>*</sup> 100.4	99.5	96.5	98.8	92.8
240	—	99.0	— <sup>*</sup> 94.0	97.1	92.5
250	—	97.6	—	— <sup>*</sup> 93.9	92.2
260	—	— <sup>*</sup> 95.0	—	—	90.7
270	—	—	—	—	— <sup>*</sup> 86.5
280	—	—	—	—	—
Critical tem- perature .....	233° 7	264° 85	250° 1	257° 4	276° 2
Average $\mu'$ .....	109.59	98.79	98.88	99.02	93.12
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	103.6	93.7	91.7	92.4	84.1

TABLE I. (continued).

Mean $\mu'$ .....	Ethyl propionate 91.97.	Methyl butyrate 91.17.	Methyl isobutyrate 87.78.	Water 558.1.	Methyl alcohol 302.3.	Ethyl alcohol 240.1.
Temperature 0° C.	+ * 96.1	+ * 96.5	+ * 92.5	+ * 574.7	304.7	- * 232.8
10	—	—	—	+ * 571.4	306.0	— 235.4
20	—	—	—	+ 567.5	306.6	— 237.4
30	—	—	—	+ 564.1	307.9	239.9
40	—	—	—	+ 561.5	307.4	241.7
50	—	—	—	559.1	+ 308.3	242.4
60	—	—	—	556.7	308.0	+ 243.6
70	—	—	—	554.9	308.1	+ 244.1
80	—	—	—	553.4	307.8	+ 244.9
90	+ 93.1	—	89.2	552.4	307.1	+ 244.6
100	+ 93.5	90.9	89.3	551.3	306.3	+ 244.8
110	+ 93.2	90.8	89.0	550.0	306.0	242.7
120	+ 93.0	90.8	88.7	548.4	305.4	242.1
130	92.5	90.6	88.8	547.5	304.5	241.0
140	91.7	91.0	88.8	547.1	304.1	241.0
150	91.3	91.0	88.6	547.1	301.3	241.1
160	90.9	90.8	88.4	547.4	303.1	239.8
170	90.6	90.7	88.3	548.6	302.3	238.2
180	90.4	90.9	88.3	549.9	300.9	236.5
190	90.6	91.2	88.5	552.0	300.8	— * 233.3
200	90.7	91.7	88.9	554.3	299.3	— * 230.0
210	91.1	91.9	89.0	554.8	— * 295.4	— * 226.3
220	91.4	91.8	88.9	560.4	— * 287.6	— * 223.0
230	91.4	+ 92.3	88.8	+ 561.0	— * 276.5	— * 219.7
240	91.5	+ 92.4	88.3	+ 562.1	— * 237.4	— * 209.2
250	91.4	+ 93.0	87.7	+ 560.9	—	—
260	90.4	+ 92.5	86.2	558.3	—	—
270	— * 86.7	91.2	—	+ 561.2	—	—
280	—	— * 84.2	—	—	—	—
Critical tem- perature .....	272° 9	281° 3	267° 55	370°	240° 0	243° 1
Average $\mu'$ .....	91.59	91.31	88.45	555.1	305.04	240.90
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	80.8	84.3	82.0	—	262.4	179.9

TABLE I. (*continued*).

Mean $\mu'$ .....	Propyl alcohol 199.2.	Acetic acid.	Carbon disulphide 82.41.	Chloro- form 57.97.	Acetone 150.8.
Temperature	+				
0° C.	203.1	—	82.2	58.0	150.8
10	—	—	82.4	57.9	150.7
20	—	81.3	82.5	57.8	150.7
30	—	83.8	82.6	57.8	150.8
40	—	86.1	82.7	57.4	149.7
50	—	87.8	82.8	57.9	151.1
60	—	90.4	82.8	58.0	151.2
70	—	92.2	82.8	—	—
80	199.9	94.7	82.8	—	—
90	199.2	96.4	82.7	—	—
100	197.6	98.5	82.6	+ 59.0	151.3
110	196.2	100.7	82.5	—	—
120	— *	104.3	82.2	—	—
130	193.6	104.9	81.9	—	—
140	— *	105.5	81.6	—	—
150	191.3	106.6	81.2	—	—
160	— *	107.9	—	—	—
170	185.6	111.7	—	—	—
180	— *	111.3	—	—	—
190	184.1	113.3	—	—	—
200	— *	115.4	—	—	—
210	178.6	117.5	—	—	—
220	— *	119.1	—	—	—
230	176.6	121.5	—	—	—
240	— *	124.1	—	—	—
250	173.2	126.4	—	—	—
260	— *	128.4	—	—	—
270	168.8	130.0	—	—	—
280	— *	131.2	—	—	—
290	164.1	131.2 <sup>1</sup>	—	—	—
Critical tem- perature .....	263°·7	321°·65	273°·05	260°·0	237°·5
Average $\mu'$ .....	199.2	—	82.41	57.97	150.8
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	143.7	150.7	98.8	—	—

<sup>1</sup> At 300°=130.0; 310°=127.4; 320°=122.2.

TABLE I. (continued).

Mean $\mu'$ .....	Ammonia 381.9.	Sulphur dioxide.		Carbon dioxide 95.2.	Nitrous oxide 88.3.
		85.80.	85.80.		
Temperature -30° C.	381.5	—	—	94.6	—
-20	380.9	—	—	+ 96.3	— 82.5 *
-10	380.6	+ 87.4	+ * 88.6	95.8	— 87.0
0	380.5	+ 86.8	+ 87.0	95.4	+ * 90.7
10	381.1	84.2	85.5	— 93.7	+ * 90.5
20	382.2	84.1	— 84.3	— * 90.5	— * 84.9
30	383.2	84.4	— * 82.7	— * 61.4	— * 62.5
40	385.1	84.6	— * 81.1	—	—
50	—	— * 81.6	— * 80.1	—	—
60	—	— * 83.0	— * 77.8	—	—
70	—	85.8	—	—	—
80	—	+ * 88.1	—	—	—
90	—	+ * 88.9	—	—	—
100	—	+ * 87.5	—	—	—
110	—	+ 86.6	—	—	—
120	—	+ * 87.6	—	—	—
130	—	+ * 89.2	—	—	—
140	—	+ * 91.4	—	—	—
150	—	+ * 94.2	+ * 95.3	—	—
Critical tem- perature .....	131° 0	156° 0	156° 0	31° 35	38° 8
Average $\mu'$ .....	381.86	85.48	85.6	95.16	—
$\mu'$ from $\frac{dP}{dT} = \frac{2R}{V}$	—	85.4	85.4	91.8	93.6

substance is shown at the top of the table. All divergences of more than 2 per cent. from the mean value given are marked with a \* above and to the right. All divergences of more than 1 per cent. are marked above and to the left with a

+ or - to indicate the character of the divergence. The average value of the unstarred results is shown at the bottom of the table.

The most casual examination of the table verifies at once the substantial truth of the equation for most of the substances examined. A detailed discussion of the data and results is given in the papers above cited. Here I would only point out that in the first twenty-six substances shown in the table, for which the very accurate measurements made by Dr. Sydney Young\* and his co-workers were available, there is not a single divergence from the mean value of the constant greater than 2 per cent. except at 0° C. and near the critical temperature and with di-isobutyl. Eight of the substances show not a single divergence within the limits stated greater than 1 per cent. Di-isobutyl was quite possibly impure when measured. At 0° (30° for brom-benzene and iodo-benzene) and near the critical temperature, unusually large errors, for a discussion of which see the papers cited, are unavoidable in obtaining the values of the constants. The errors of measurement are always compounded and often multiplied in their effect upon the constant. The associated substances, water, the alcohols, and acetic acid, should not give a constant and do not. For the last seven substances shown in the table the data obtainable are not always trustworthy. After careful consideration of the facts upon which these statements are based (see the papers cited) I have no hesitation in saying that the constant is as near a constant as the errors of observation in the measurements used will permit, and I regard the substantial truth of the equation as established beyond question.

It would be quite impossible within the limits of this paper to discuss the data used in detail and the important consequences that follow from the equation. Most of the data used were obtained from the measurements of Dr. Sydney Young and his co-workers, and I am deeply indebted to Dr. Young for extensive information regarding the data and for obtaining in advance of their publication (see reference cited) his extensive revision of much of the data used in my earlier papers and by Kleeman. The series of papers cited contain the details and the discussion and a complete republication of all of that work is contemplated some time in the future. Suffice it to say here that a comparison of the results of equation 1 with the corresponding equation proposed by Kleeman on the supposition of an *inverse fifth power*

\* Sci. Proc. Royal Dublin Society, xii. p. 374 (1910).

*law* leaves no room whatever for doubt that the relation of Kleeman is not supported by the facts. The variation in the constant of Kleeman's equation cannot be attributed to the data, which are far too accurate to permit of the variations noted, and it is not due (as Kleeman supposes) to the influence of temperature upon the attraction. The possible influence of temperature upon chemical affinity has been specially studied by the author\* for the reaction  $\text{H}_2 + \text{O} = \text{H}_2\text{O}$ , and the evidence is overwhelmingly against the idea that temperature changes the *chemical* attraction. The constancy of the results detailed in Table I. is itself evidence that temperature is without influence on *molecular* attraction, and this fact will appear more clear when the extensive discussions cited are considered. The probable mutual relation of temperature and molecular attraction is discussed in Part III. of this article.

PART II.—*The Relation of Dieterici*,  $\lambda = CRT \ln \frac{d}{D}$ .

In this relation C is a constant, nearly, but not quite, the same for all substances; R is the usual gas constant; T denotes absolute temperature; the other symbols are as given before.

This relation was proposed and discussed by Dieterici† and later by Richter‡, and has been thoroughly investigated by the author§. Kleeman investigated this equation||, using data (which data have since been subject to some corrections by Young) from an earlier paper by the author, and has overlooked entirely the discussion of this equation by the author. (Perhaps I was at fault in publishing these physical relations in journals devoted mainly to chemistry.) I therefore republish in Table II. a summary of the results obtained..

In this table all values of C differing by more than 2 per cent. from the average value of the uncrossed results shown at the top of the column are marked with an asterisk above and to the right. All values of C differing from this average value of C by more than 1 per cent. are marked with a plus or minus, above and to the left, to show the nature of the divergence.;

\* Trans. Amer. Electrochemical Soc. xiv. p. 35 (1908).

† *Ann. der Physik*, (4) xxv. p. 569 (1908).

‡ *Inaugural-Dissertation*, Rostock, 1908, "Ueber die innere Verdampfungswärme."

§ Journ. Amer. Chem. Soc. xxxi. p. 1099 (1909).

|| Phil. Mag. xx. p. 665 (1910).

TABLE II.—Values of C.

Av. C. Temp.	Ethyl oxide.	Di-iso- propyl.	Di-iso- butyl.	Isopen- tane.	Normal pentane.	Normal hexane.	Normal heptane.	Normal octane.	Hexa- methylene.	Benzene.	Fluor- benzene.
0°	1.724	1.725	1.813	1.688	1.707	1.752	1.814	1.858	1.694	1.690	1.711
20	1.718	1.672*	1.669*	1.696	1.697	1.680*	1.685*	1.694*	1.606*	1.601*	1.599*
40	1.714	...	...	1.680	...	...	...	...	...	...	...
60	1.712	...	...	1.682	...	...	...	...	...	...	...
80	1.718	1.726	...	1.678	1.707	1.734	...	...	...	...	...
	1.721	1.734	...	1.682	1.710	1.753	1.800	...	1.709	1.693	1.724
100	1.732	1.727	1.791*	1.691	1.711	1.759	1.809	...	1.710	1.691	1.733
120	1.737	1.725	1.779*	1.692	1.724	1.767	1.808	1.813*	1.702	1.678	1.724
140	+ 1.749	1.721	1.763*	1.694	1.713	1.760	1.800	1.826	1.691	1.684	1.710
160	+ 1.742	1.720	1.769*	1.691	1.708	1.752	1.801	1.833	1.685	1.693	1.702
180	1.700	1.722	1.794	1.648*	1.696	1.751	1.823	1.841	1.689	1.701	1.699
200	...	1.723	1.810	...	...	1.755	+ 1.835	1.848	1.680	1.697	1.696
220	...	1.679*	1.831	...	...	1.735	+ 1.847	1.866	1.692	1.698	1.706
240	...	...	+ 1.858*	...	...	...	+ 1.858*	1.873	1.696	1.693	1.715
260	...	...	+ 1.877*	...	...	...	1.820	+ 1.895	1.699	1.691	1.724
280	...	...	...	...	...	...	...	+ 1.889	...	1.665	1.688
Critical temp.	193°·8	227°·35	276°·8	187°·8	197°·2	234°·8	260°·85	296°·2	280°·0	288°·5	286°·55



TABLE II.—Values of C (*continued*).

Av. C. Temp. °	Chloro- benzene.	Bromo- benzene.	Iodo- benzene.	Carbon tetrachloride.	Stannic chloride.	Methyl formate.	Ethyl formate.	Methyl acetate.	Propyl formate.	Ethyl acetate.	Methyl propionate.
20	1.714	1.691	1.687	1.667	1.741	1.706	1.747	1.784	1.774	1.812	1.803
40	1.583*	1.603*	1.558*	1.592*	1.579*	1.717	1.695*	1.703*	1.679*	1.721*	1.703*
60	...	...	...	...	...	1.720	...	...	...	...	...
80	...	...	...	...	...	1.713	1.757	1.778	...	...	...
100	...	...	...	1.662	1.742	1.706	1.758	1.790	1.785	1.798	1.791
120	...	...	...	1.664	1.749	1.702	1.756	1.784	1.777	1.816	1.796
140	1.681	...	...	1.662	1.746	1.714	1.754	7.786	1.774	1.821	1.800
160	1.697	1.658	...	1.658	1.745	1.706	1.750	1.790	1.776	1.819	1.803
180	1.711	1.675	1.658	1.665	1.748	1.696	1.743	1.792	1.766	1.806	1.805
200	1.713	1.688	1.679	1.663	1.735	1.677	1.739	1.778	1.765	1.813	1.805
220	1.723	1.701	1.697	1.674	1.739	1.616*	1.718	1.771	1.775	1.821	1.818
240	1.733	1.698	1.701	1.683	1.739	...	1.663*	1.731*	1.788	1.806	1.818
260	1.731	1.707	1.696	1.685	1.736	...	...	...	1.789	1.755*	1.788
280	...	...	...	1.657	1.733	...	...	...	1.740	...	...
Crit. temp.	359.1	397.0	448.0	283.15	318.7	214.0	235.3	233.7	264.85	250.1	257.4

TABLE II.—Values of C (continued).

Av. C. Temp. °	Propyl acetate.	Ethyl propionate.	Methyl butyrate.	Methyl isobutyrate.	Water.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Acetic acid.	Carbon disulphide.	Chloro- form.	Acetone.
	1·850 — 1·718*	1·837 — 1·718*	1·824 — 1·709*	1·814 — 1·711*	...	...	...	...	...	1·516	1·706 — 1·676	1·754 — 1·728
20	...	...	...	...	1·559	1·735	1·855	...	0·857	1·516	1·696	1·750
40	...	...	...	...	1·581	1·784	1·948	...	0·925	1·524	1·716 +	1·754 +
60	...	...	...	...	1·601	1·825	2·018	...	0·986	1·528	1·735	1·786
80	...	...	...	...	1·620	1·858	2·080	2·103	1·047	1·525	...	...
100	1·834	1·844	1·779*	1·807	1·637	1·877	2·124	2·135	1·101	1·517	+	1·802*
120	1·848	1·846	1·790	1·805	1·648	1·896	2·140	2·137	1·177	1·503	...	...
140	1·845	1·832	1·802	1·813	1·659	1·906	2·157	2·148	1·198	— 1·482*	...	...
160	1·853	1·823	1·804	1·810	1·670	1·918	2·170	2·117	1·231	...	...	...
180	1·856	1·817	1·809	1·811	1·684	1·919	2·161	2·102	1·275	...	...	...
200	1·858	1·827	1·828	1·825	1·702	1·927	2·127	2·073	1·326	...	...	...
220	1·862	1·843	1·834 +	1·828	1·723	1·876	2·094	2·030	1·373	...	...	...
240	1·857	1·854	1·849 +	1·824	1·726	...	2·011	1·948	1·431	...	...	...
260	1·835	1·848	1·800	1·800	1·717	...	...	1·879	1·481	...	...	...
280	...	...	1·737*	...	...	...	...	...	1·517	...	...	...
Crit. temp.	276°·2	272°·9	281°·3	267°·55	370°·0	240°·0	243°·1	263°·7	321°·65	273°·05	260°·0	237°·5

TABLE II.--Values of C (continued).

	Ammonia.	Sulphur dioxide.	Carbon dioxide.	Nitrous oxide.
Av. C. Temp.	1·622	1·707	1·762	1·513
—30°	1·608	...	— 1·738	...
—20	1·615	...	+ 1·789	1·503
—10	...	1·712	...	...
0	1·622	1·712	1·760	+ 1·637 *
20	1·629	1·679	— 1·682 *	1·521
40	1·634	1·697	...	...
60	...	— 1·670 *	...	...
80	...	+ 1·750 *	...	...
100	...	+ 1·724	...	...
120	...	+ 1·736	...	...
140	...	+ 1·818 *	...	...
Crit. temp. ...	131° 0	156° 0	31° 35	38° 8

The results shown in Table II. justify the conclusion that *at very low vapour pressures the equation  $\lambda = CRT \ln \frac{d}{D}$  proposed by Dieterici is not exactly true. The remarkable, and apparently exact, agreement with the facts given by this equation at higher temperatures deserves the closest attention and study.*

For a discussion of this equation the papers by Dieterici, Richter, and the author, already cited, should be consulted, and a later study by W. Steinhaus\* has just appeared. The equation undoubtedly marks an important step forward, and must aid greatly in understanding the theory of liquids.

PART III.—*The Relation of Temperature and Molecular Attraction.*

In the series of papers cited I have held that the most direct and natural interpretation to give equation 1 is that it is caused by a force among the individual molecules following the law

$$f = \frac{\mu m}{s^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2)$$

\* *Inaugural-Dissertation*, Kiel, 1910, "Studien zum Problem der Zustandsgleichung."

where  $\mu$  is a constant for any given species of molecule,  $m$  is the mass of the molecule, and  $s$  is the average distance apart of the molecules. This interpretation considers the attractive force of a given molecule as a definite and constant property of the molecule, not capable of *indefinite* multiplication by the introduction of other molecules into the surrounding space. This definite force is absorbed or used up at an average distance  $s$  depending upon the distance apart of the molecules. This view is fully discussed in the article in the Journ. Phys. Chem., May 1911.

If the law of the molecular force is known it would seem on first inspection a simple matter to write the general equation of state for any substance, but such is by no means the case. Temperature has *per se* no influence upon the molecular attraction. The constancy of the results shown at different temperatures in Table I. for the substances examined is conclusive evidence upon that point. But it should be noted that while equation 1 is tested for each substance over a very wide range of temperature, yet during each individual test the temperature is constant, since the substance tested each time simply changes from liquid to vapour *under a definite pressure and at a definite temperature*. While, therefore, the constancy of the results at different temperatures as shown in Table I. is conclusive evidence that the change of temperature in the substance has not changed the attractive force operating between the molecules, yet *the temperature has been one factor determining the vapour pressure and the densities of liquid and vapour at each temperature*. The question to be now considered is, In what way does the effect of temperature combine with the law of molecular attraction in order to produce a given density under a given pressure?

The problem is by no means easy of solution for reasons that will later appear. It seems best, therefore, first to consider carefully and fully the energy relations of two masses governed by the law of attraction given. Then later to apply the knowledge obtained, so far as can be done, to  $n$  masses.

The law given in equation 2 for the molecular force differs in some respects from the law of gravitation, and yet I have stated at length\* reasons for believing that both the molecular force and the gravitational force are identical in origin and character and are governed by the same law. It is not possible to go into this discussion here further than to say that the law given in equation 2 deals with the totality of the force of a given molecule or mass, while Newton's law

\* Journ. Phys. Chem., May 1911.

of gravitation shows how this total force is distributed among various masses. In considering the problem of two bodies it will greatly shorten the necessary discussion to consider that they are governed by the gravitational law of force, since the consequences of both laws, so far as they concern the point under discussion, are identical. The problem of two bodies under the influence of the gravitational attraction has of course been completely solved, and the relations pointed out below are therefore not new. But certain of the applications made of these recognized mechanical consequences are new so far as I am aware. At any rate it is certain that the idea that molecular attraction is affected by temperature is so widespread, and has been considered such a necessary deduction from so many facts, that every precaution must be taken to set forth clearly their true relationship. For this reason I state the various steps involved, though leaving the reader to obtain the proof of the more fundamental statements from any suitable work on analytical or celestial mechanics.

It will be assumed that the two bodies are spheres and homogeneous in concentric layers. It will also be assumed that the two bodies, and every particle of the two bodies, are subject to the action of a force  $f$ , which obeys the law of gravitation as proposed by Newton :

$$f = -k \frac{m_1 m_2}{s^2}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $m_1$  and  $m_2$  are the masses of the two attracting particles,  $s$  is their distance apart, and  $k$  is a constant. It can then be shown that :—

1. The attraction of the two bodies will act as though it proceeded from the centres of the spheres, and will be proportional to the respective masses of the spheres, and will vary inversely as the square of their distance apart.

2. Whatever the relative motion of the two spheres may become, the centre of mass of the two spheres will retain its original condition, remaining either at rest or moving in a straight line with constant speed.

3. The force of attraction will cause the two bodies to describe similar conics around their common centre of gravity.

4. The motion of one body with respect to the other is in a plane passing through the centre of the other.

5. The mass  $m_1$  will move with reference to the centre of mass  $m_2$  precisely as if its mass had been added to the mass

of  $m_2$ , while itself had become a mere particle. This relative orbit will in all respects be like the actual one around the centre of gravity, only magnified in the proportion  $\frac{m_1+m_2}{m_2}$ . To reduce the relative orbit of  $m_1$  to the true orbit, the proportions of the relative orbit must therefore be multiplied by  $\frac{m_2}{m_1+m_2}$ . The velocity  $v_1$  of  $m_1$  obtained at any point of its relative orbit must be multiplied by the same factor in order to obtain its true velocity. In order to obtain the true energy  $E_1$  of  $m_1$  its velocity squared at any point of its relative orbit must be multiplied by  $\frac{1}{2} \frac{m_1 m_2^2}{(m_1+m_2)^2}$ . Similar relations hold for the motion of particle  $m_2$  around the centre of  $m_1$ .

6. The force governing the motion of the two bodies can therefore be regarded as proceeding from the centre of either body, the other being reduced to a mere particle, and the force would be measured by

$$f = -k \frac{m_1+m_2}{s^2} = \frac{-\epsilon}{s^2}. \quad . \quad . \quad . \quad (4)$$

$\epsilon$  is used to denote  $k(m_1+m_2)$ . Later in this article I speak of this centre of force as the centre of mass. This is not, strictly speaking, correct, but the transformation is easily made as already described.

7. Since energy  $= \int f \cdot ds$ , the energy changes involved in bringing the particles from distance  $s_2$  to distance  $s_1$  is

$$- \int_{s_2}^{s_1} k \frac{m_1 m_2}{s^2} \cdot ds = k m_1 m_2 \left( \frac{1}{s_1} - \frac{1}{s_2} \right). \quad . \quad . \quad (5)$$

If  $s_2 = \infty$  then this expression becomes  $\frac{k m_1 m_2}{s_1}$ . That is to say, the energy given out as two bodies approach each other, multiplied by the distance apart of the bodies, is equal to a constant which depends on the product of the masses of the two bodies :

$$E_{\infty} \cdot s = k m_1 m_2. \quad . \quad . \quad . \quad . \quad (6)$$

8. If we consider the mutual interaction of two bodies in space we might consider that the force acting between these bodies was of a mutual character, and that it acted continuously on both bodies. The question, Will the same

force acting for the same time on two different masses produce in the masses the same amount of kinetic energy? would therefore seem to be a perfectly proper question. But on analysis it will be seen that the question cannot be directly answered from the usual standpoint. For  $fs = E$  and  $ft = mv$ ,  $t$  denoting time. When using the usual nomenclature we can therefore only speak of the force between the bodies as acting through a certain distance when producing energy, and can consider it as acting for a certain time only with reference to the momentum produced.

As two bodies come together from an infinite distance under their mutual attraction, kinetic energy is not developed equally in the two bodies. For the force acting on the two bodies is the same. Now  $f = ma$ , where  $a$  is the acceleration produced, and  $ft = mat$ . Since  $a = v/t$ , we have  $ft = mtr/t = mv$ . But  $ft$  is the same for each body. Therefore

$$m_1 v_1 = m_2 v_2. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now the energy of mass  $m_1$  when moving with velocity  $v_1$  is  $1/2 m_1 v_1^2$ , and similarly for the energy of mass  $m_2$  we have  $1/2 m_2 v_2^2$ , and

$$1/2 m_1 v_1^2 + 1/2 m_2 v_2^2 = \frac{k m_1 m_2}{s}.$$

Substituting for  $v_2$  its value from equation 7, we have

$$1/2 m_1 v_1^2 \left( \frac{m_1 + m_2}{m_2} \right) = \frac{k m_1 m_2}{s},$$

and therefore

$$\left. \begin{aligned} E_1 &= 1/2 m_1 v_1^2 = \frac{m_2}{m_1 + m_2} \cdot \frac{k m_1 m_2}{s} = \frac{k m_1 m_2^2}{m_1 + m_2} \cdot \frac{1}{s} \\ E_2 &= 1/2 m_2 v_2^2 = \frac{m_1}{m_1 + m_2} \cdot \frac{k m_1 m_2}{s} = \frac{k m_1^2 m_2}{m_1 + m_2} \cdot \frac{1}{s} \end{aligned} \right\}. \quad (8)$$

It should be noticed that we have answered the question above asked only by introducing an experimental fact, namely, that masses mutually determine in each other accelerations inversely proportional to the masses accelerated. From equation 8,  $E_1 m_1 = E_2 m_2$ , a result that follows at once from equation 7.

9. It is convenient to consider the orbit of the smaller body with reference to the centre of mass of the larger body. Considering the most general case, that is where the body

has an initial velocity of projection,  $v_3$ , the velocity acquired,  $v$ , is governed by the following law :—

$$v^2 = v_3^2 + 2\epsilon \left( \frac{1}{s_1} - \frac{1}{s_2} \right). \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The path pursued by the body with reference to the centre of mass chosen (the centre of the larger body) will be an ellipse (or its limiting case a circle), a parabola (which marks the boundary between the ellipse and the hyperbola), or hyperbola (or its limiting case a straight line), according as  $v_3^2$  is less than, equal to, or greater than  $\frac{2\epsilon}{s_2}$ . The increase of velocity caused by the approach of the body towards the centre from any distance is independent of the initial velocity of the body, or of the path pursued between  $s_1$  and  $s_2$ , but depends solely on the magnitudes  $s_1$  and  $s_2$ , and is given by the expression

$$v^2 - v_3^2 = 2\epsilon \left( \frac{1}{s_1} - \frac{1}{s_2} \right). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

10. Assuming that the body is initially at rest at an infinite distance from the centre of mass, equation 10 takes the form

$$v^2 = \frac{2\epsilon}{s_1}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If  $s_1$  becomes zero, then the velocity acquired would be infinite. The distance between the centres of the bodies could not become zero. It is probable that the speed gained by the bodies as they approached would cause Newton's law to be disobeyed, and that even the surfaces of two ordinary particles could not come into actual contact with each other.

If  $s_2 = 2s_1$ , then equation 10 gives

$$v^2 = \frac{\epsilon}{s_1}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

That is, a body acquires as much energy in falling from  $2s_1$  to  $s_1$  as in falling from infinity to  $2s_1$ .

11. The energy abstracted from the æther is proportional to the square of the velocity which the body gains due to the action of the attractive forces, and is equal to one-half the mass of the body times the square of the velocity gained. It is perhaps hardly necessary to point out that if the body starts at an infinite distance from the centre of mass it cannot follow an elliptical or circular orbit in approaching, or with



reference to, the centre of mass, unless the body loses to some third body some of its kinetic energy. This follows

because if its total velocity at any point is so great as  $\frac{2\epsilon}{s_1}$

it will, as remarked under 9, necessarily follow a straight line, parabola, or hyperbola, as its path, and will eventually return to the infinite distance at which it started. If, therefore, the body starts from rest at an infinite distance from the centre of mass, the total velocity gained by the body, due to the action of the attractive force, is given by equation 11, and this equation is equally true for any path (parabola, hyperbola, or straight line) which the body may take in approaching the centre of mass, as can be seen from equation 10. The statement already made under section 7 holds good, therefore, under all circumstances, and is quite independent of the paths pursued by the bodies during their approach.

*If two bodies under the action of Newton's law of gravitation start originally at an infinite distance apart, the total amount of potential energy of the æther which may be transformed into kinetic energy by the approach of the bodies is, under all circumstances, inversely proportional to the final distance of the bodies from each other, and is given by the equation*

$$E_{\infty} = \frac{km_1m_2}{s}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

12. From section 11 it follows that in order that a body, acting under gravitational attraction, should move in a circular, or elliptical, or limited linear orbit, it is necessary that it should part with some of the energy which it would have attained had it assumed its position in the orbit by falling from an infinite distance. Since only mathematically can two bodies with infinite orbits be regarded as forming a stable system, we may further state :

*Any two bodies forming a stable system under the action of gravitational attraction must have lost to some third body a part of the kinetic energy which they obtained from the æther in assuming that position of equilibrium.*

13. The amount of energy surrendered to a third body may easily be found for any particular orbit from the following considerations :—

The period of a body is the same whether it moves in a circle, in an ellipse, or in a straight line, and is given by the expression

$$P_{1,2} = \frac{2\pi a^{3/2}}{\sqrt{\epsilon}}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where  $a$  denotes the radius of a circular orbit, or the major semi-axis of an elliptical orbit, or one-half the distance from the centre to the point of return on the linear orbit (one-fourth of the total orbit).

14. Since the circumference of a circular orbit is  $2\pi a$ , and the velocity  $= \frac{\text{circumference}}{\text{period}}$ , it follows that for a body moving in a circular orbit

$$v = \frac{2\pi a \sqrt{\epsilon}}{2\pi a^{3/2}} = \sqrt{\frac{\epsilon}{a}} \quad \text{and} \quad v^2 = \frac{\epsilon}{a} \quad . \quad . \quad . \quad (14)$$

Now the velocity squared, acquired by the same body in falling from an infinite distance to its circular orbit is given by equation 11 and is  $2\epsilon/a$ . Evidently, therefore, one-half of the total energy acquired by the body must have been transferred to some third body before it could assume its stable circular orbit, and we can state:

*Two bodies moving in circular orbits around their common centre of mass under the action of gravitation before they could assume this position of stable equilibrium must have surrendered to some outside third body one-half of the kinetic energy which they gained from the ether by their approach.*

15. The speed of a body moving in an ellipse is at every point equal to that which it would acquire in falling from the circumference of a circle, with centre at the origin and radius equal to the major axis of the conic, to the ellipse. For the velocity when moving in an elliptical orbit is given by

$$\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 = v^2 = \epsilon \left(\frac{2}{s_1} - \frac{1}{a}\right), \quad . \quad . \quad . \quad (15)$$

where  $s_1$  is the distance from the origin and  $a$  is the major semi-axis. From equation 10, making the velocity in the orbit equal the velocity acquired in falling from  $s_2$ , we have

$$\epsilon \left(\frac{2}{s_1} - \frac{1}{a}\right) = 2\epsilon \left(\frac{1}{s_1} - \frac{1}{s_2}\right). \quad . \quad . \quad . \quad (16)$$

Therefore the energy retained by a body moving in an elliptical orbit is equal to the energy that it would acquire in falling into its orbit from a distance from its centre of mass equal to the major axis,  $2a$ , of its orbit. The body must have previously surrendered to some third body an amount of energy equal to that which it would acquire in moving from an infinite distance from the centre of mass to

the distance  $2a$ . The velocity acquired by such motion is given by equation 11 as  $v^2 = \frac{\epsilon}{a}$ , and the energy acquired by the body and surrendered to some third body before it could assume its stable elliptical orbit is  $\frac{m\epsilon}{2a}$ . But exactly this amount of energy must be abstracted from a body in order that it shall move in a circular orbit of radius  $a$ . We may therefore state:

*A body moving in an elliptical orbit under the action of gravitational attraction can be made to move in a circular orbit whose radius is equal to the major semi-axis of the elliptical orbit without adding to, or subtracting from, the kinetic energy of the body.*

16. The limited linear orbit is a special case of the ellipse, just as the infinite line was a special case of the hyperbola.

The total length of the orbit is  $4a$ , the period is  $\frac{2\pi a^{3/2}}{\sqrt{\epsilon}}$ , and therefore the average velocity (as regards time) in the orbit is  $\frac{2}{\pi} \sqrt{\frac{\epsilon}{a}}$ . The actual velocity has varying values from zero to infinity. The body in falling from infinity to the distance  $2a$  from the centre of mass must have received, according to equation 11, a velocity such that  $v^2 = \frac{\epsilon}{a}$ . Now

in the linear orbit, conceived as commencing at  $2a$  and extending to the centre and then returning, its velocity at the point  $2a$  is zero. By equation 12 the body will have regained as much velocity in falling from  $2a$  to  $a$  as it gave out in falling from infinity to  $2a$  when it was brought to rest at  $2a$ . Clearly, therefore, *we can substitute for a linear orbit a circular orbit of radius equal to one-fourth of the total linear orbit without changing the energy conditions of the body.*

17. The arithmetical mean distance of a body from the centre of mass, when the body is moving in a linear orbit whose origin is distant  $2a$  from the centre of mass, is  $a$ . Similarly when the body is moving in an elliptical orbit the arithmetical mean distance from the centre of mass is the major semi-axis  $a$ . Therefore we can state as the result of the discussions under 14, 15, and 16, that

*The energy given out by any two bodies originally at rest at an infinite distance apart in forming any stable configuration under the action of gravitational attraction is equal to the kinetic energy which they retain and is, for either body, inversely*

proportional to its mean distance from their common centre of mass.

If we designate the kinetic energy of motion in its orbit at this mean distance from the centre of mass retained by particle  $m_1$  as  $E_{10}$  and the energy lost as  $E_{1L}$ , and similarly for particle  $m_2$ , we shall have, when  $E_a$  denotes the total attractive potential energy obtained from the æther:

$$E_a = E_{10} + E_{1L} + E_{20} + E_{2L} = \frac{km_1m_2}{s} \quad . \quad . \quad (17)$$

$$\left. \begin{aligned} E_{1L} = E_{10} &= 1/2 \frac{km_1m_2^2}{m_1+m_2} \cdot \frac{1}{s} \\ E_{2L} = E_{20} &= 1/2 \frac{km_1^2m_2}{m_1+m_2} \cdot \frac{1}{s} \end{aligned} \right\} \quad . \quad . \quad . \quad (18)$$

These equations govern the energy relations of two masses in stable equilibrium under all circumstances.

18. If we supply a given amount of energy, say  $E_k$ , to a system with a circular orbit, or in fact with any orbit, then the exact orbit followed will depend upon the exact way in which the energy is added. Since the amount of "lost" energy is decreased by this addition of energy to the system, and since  $E_0 = E_L$ , the amount of orbital energy must also be decreased. That is to say, the major semi-axis, or the radius, must be increased, and the potential energy must be increased by an amount equal to  $2E_k$ , one-half of this amount being added to the system and one-half coming from the decrease of the mean orbital velocity in the system. The mean orbital kinetic energy of the system can only be increased by abstraction of energy—not by addition of energy. This remarkable fact may be a well-known mechanical consequence of the motion of two bodies under the gravitational law of attraction, but its significance does not seem to have been appreciated by those trying to express the relationship between temperature and molecular attraction. For the above fact leads at once to the question: *How can the temperature of a system of two bodies be increased by the addition of energy, since addition of energy seems to necessitate a loss of mean orbital velocity?* We might as well go to the bottom of the trouble at once. We have no generally accepted definition of temperature, or better, perhaps, no generally accepted idea of temperature that will apply to a system under the influence of attractive forces. If there are no attractive forces then what we call temperature is proportional to, and is measured by, the kinetic energy of the moving particles (molecules). But if attractive forces exist, this definition of temperature no longer

holds good. Some few people have been misled into thinking that Clerk Maxwell's investigation of the distribution of velocity in a system of moving particles applies to a system under the influence of attractive forces, but such is not the case. The mistake has arisen because the investigation is sometimes quoted with no very clear statement of the fundamental suppositions of the mathematical investigation, and because the investigation has been shown to apply to composite molecules *if there is no residual attraction between the molecules*. But if there is molecular attraction, Clerk Maxwell's investigation will not apply.

It is worthy of note that if, after the addition of energy amounting to  $E_k$ , the new orbit assumed be spherical, the new velocity will, as stated, be less than it was before by  $E_k$ . Now if, by any arrangement, the body could be held in its new orbit, and its temperature (velocity squared) increased to  $E_k$  greater than its original temperature (velocity squared), then the total energy necessary for this purpose would be  $3E_k$ . I mention this because it might have some connexion with the fact that the total energy required to bring most metals into the molten condition at their melting point is very approximately three times the energy that would be necessary to raise a perfect monatomic gas of the same molecular weight to the same temperature.

19. The absurdity of trying to define temperature as the kinetic energy of the particles in a system under the influence of attractive forces can be seen if the chemical reaction  $H_2 + O = H_2O$  is considered. I have shown\* that the 16 grams of oxygen and the 2.016 grams of hydrogen taking part in the above reaction, together at  $-273^\circ C.$  occupy 34.78 c.c., and when occupying this volume at that temperature they contain 67,300 calories more of energy than does the 18.016 grams of ice which they form if united, and which occupies a volume of 19.21 c.c.

There is no supposition whatever connected with this fact, except the slight uncertainty due to the measurements and their extrapolation, and this uncertainty is probably not greater than 100 calories. The total energy possessed by the hydrogen and oxygen at  $-273^\circ C.$  is probably very much more than 67,300 calories, and may be many times that amount, for we have no evidence whatever as to the energy which the ice possesses at that temperature. We only know that the energy of the ice is 67,300 calories less than the amount possessed by the equivalent hydrogen and oxygen before the combination. The ice may, and in our opinion

\* Trans. Amer. Electrochemical Society, xiv. p. 35 (1908).

certainly does, possess a vast store of energy. Its store of energy is perhaps comparable to that possessed by radium.

In what form does the 67,300 calories of energy possessed by the 34.78 c.c. of hydrogen and oxygen at  $-273^{\circ}$  C. exist? If the same mechanical laws which govern larger masses of matter and energy at higher temperatures apply to the hydrogen and oxygen at  $-273^{\circ}$  C., then a stable system could not exist if all of the energy were kinetic, or if all of the energy were potential, but some portion of the energy must be potential and some portion must be kinetic. There has never been the slightest evidence produced to show that these mechanical laws do cease to hold at  $-273^{\circ}$  C., or with small subdivisions of mass, and therefore I think it probable that at  $-273^{\circ}$  C. the small particles—atoms if you please to call them so—of hydrogen and oxygen are in exceedingly rapid motion around their common centre of mass.

Considering the two bodies under discussion it seems clear that when they are moving in circular orbits around their common centre of mass, their orbital velocity does not constitute "temperature" motion. Two particles in such motion would constitute a stable system such as a hydrogen,  $H_2$ , or oxygen,  $O_2$ , molecule. The temperature of the system would be zero if the centre of mass were stationary.

20. If we attempt to consider how three bodies attain and maintain a system in stable equilibrium under the assumed law of force—the gravitational law—we find that mathematical analysis has as yet failed to completely solve the problem. And yet the energy relations involved can hardly be supposed greatly different from those already discussed for two bodies. It would seem fairly certain that each body in order to form a stable system would have to surrender some of the energy which it would acquire from the æther in coming into its orbital position from an infinite distance, and would retain some of this energy. The problem of four bodies is yet greatly more complicated, and it will always be impossible for mathematical analysis to follow  $n$  bodies through their mutual individual actions and orbits.

While leaving the safe ground of mathematical analysis we are yet experimentally certain that  $n$  bodies in coming together do give out a certain amount of energy, and I have shown in the papers cited\* that the energy given out ("lost") by these  $n$  bodies on coming together follows exactly the same law shown to hold for two bodies, namely:—

$$E_{\infty} \cdot s = \text{constant.} \quad . \quad . \quad . \quad . \quad (19)$$

\* See the eighth and ninth articles in the Journ. Phys. Chem. or the article in the Phil. Mag.

(The constant in this equation may not be the same constant as in equation 6, but there is no way of comparing the absolute values of the constants. Otherwise the equations are identical.) I have as yet found no satisfactory way of determining the "mean orbital" energy retained by the  $n$  molecules in coming together, but it seems certain from the constancy of the results shown in Table I. that the amount of orbital energy retained is either zero or proportional to the amount of energy given out. (In my earlier papers I expressed the opinion that the total kinetic energy of a molecule in the liquid and in the gaseous condition were the same. This statement I am now convinced was an error. The liquid molecules retain, in addition to their temperature energy, an "orbital" energy, which being proportional to the energy given out, that is to the internal heat of vaporization, was at the time undetected.)

Although certainty is impossible, it would seem pretty safe to guess that when  $n$  bodies are drawn together under the influence of their mutual attractions according to the gravitational-molecular law that:—

- a. Whatever energy is lost is lost equally by the  $n$  bodies.
- b. Whatever energy is retained is retained equally by the  $n$  bodies.

- c. When the bodies are close together, as in a liquid, the average attraction on an interior particle is balanced, but this balance of attraction is destroyed many times in a second. Any molecule is continually under the action of enormously great attractions. Its velocity must therefore be continually changing—at one instant nearly zero, at another instant probably very great. If its motion is viewed as a whole, a molecule of a liquid probably proceeds with great velocity around a more or less changing centre of mass.

We might, in line with the last sentence of section 19, consider temperature motion to be the motion of the centres of mass suggested in *c* above. But these centres of mass would usually be mere mathematical points only occasionally coinciding with a real mass. A motion of these centres of mass would therefore be in reality a motion of the individual molecules above the motion required for maintaining their equilibrium under the given attractive forces. Probably a clearer idea of the true situation can be obtained from a different standpoint.

21. Consider a circular orbit and a corresponding elliptical orbit. (By a corresponding orbit I mean an orbit that could be substituted without adding to or subtracting from the energy of the system.) The amount of energy retained

by each system is the same and the amount given up is the same. In order, therefore, to reduce either system to an unstable configuration the same amount of energy would have to be added, and it would seem that the systems must be equally stable. The area of the circle is  $\pi a^2$  and the area of the ellipse is  $\pi ab$ . The volumes of the corresponding sphere or ellipsoids of revolution are  $4/3\pi a^3$ , and  $4/3\pi ab^2$  or  $4/3\pi a^2b$ . Now  $b$  is less than  $a$ , and *if we consider the system to occupy the corresponding solids of revolution, the energy of the circular system takes up more space than the energy of the elliptical system.* This will appear yet more clear if we consider that the limit of the elliptical orbit, as  $b$  approaches zero, is the linear orbit.

The energy retained by the system per unit of space is therefore greater the more elliptical the orbit. In a system of  $n$  particles it seems to me therefore that *if we have a system with a certain amount of energy the orbits will be circular if the endeavour is to have the energy as little concentrated per unit of space as possible. If the system endeavours to concentrate the energy per unit of space as much as possible then elliptical orbits will result.*

Increase of temperature might be viewed as an increased concentration of kinetic energy in space, and we have seen that the more elliptical the orbit the more concentrated the energy per unit of volume. Apparently, therefore, only in one way could the addition of energy cause an increase of kinetic energy per unit of volume in the system and yet cause a decrease in the mean orbital energy, and that is by causing an increased ellipticity of orbit.

*A rise or fall of temperature does not change the nature or the amount of the molecular attractive force. It merely determines the orbit that the molecules will follow in obedience to the attractive force.*

22. Some light is thrown upon the relation between temperature and molecular attraction by a study of the relations at the critical temperature. In a gas indefinite expansion takes place as the pressure is decreased. This shows that the attraction between the molecules cannot be great enough to make the paths of the molecules closed curves. In a liquid, while undoubtedly many molecules whose velocity is above the average molecular velocity are continually flying away from the surface, yet it must certainly be the case that most of the molecules are drawn back by the molecular attraction. There must be for each substance a certain temperature at which the molecules attain sufficient velocity to fly apart to an infinite distance, without



condensation, if the pressure were suddenly released. This point would mark the change from elliptical to hyperbolic orbits among the particles. From section 9, for two particles, the relations between the molecular velocity  $v$ , the absolute force between the molecules which I will here call  $\mu$ , and the distance apart of the molecules  $s$ , is given by the relation

$$v^2 \frac{2\mu}{s} \dots \dots \dots (20)$$

For a system of  $n$  particles, in accordance with the ideas expressed in section 20, I believe the same relation would hold.

Now it is a common idea that at the critical temperature the kinetic energy of the molecules of a liquid (gas) under the critical pressure just balances the attraction. The idea rests on the diminution and final disappearance of surface tension at the critical temperature, and the fact that a liquid at its critical temperature may be changed to a gas without the addition of external energy, that is by an infinitesimal change in pressure, the heat of vaporization being zero. It must, then, be at this point that equation 20 will hold good. If we proceed on the supposition that the total molecular velocity at the critical temperature can be calculated as for a

perfect gas, then the velocity  $v$  is equal to  $c_1 \sqrt{\frac{T_c}{m}}$ , where  $c_1$  is a constant. The distance apart of the molecules  $s$  is equal to  $c_2 \sqrt[3]{\frac{m}{d_c}}$ , where  $c_2$  is a constant. The absolute force  $\mu$  between the molecules can be obtained from equation 1, and is, as I have shown in the papers cited, equal to  $c_3 \sqrt[3]{m\mu'}$ . Substituting these values in equation 20 we have

$$c_1^2 \frac{T_c}{m} = \frac{2c_3 \sqrt[3]{m\mu'}}{c_2 \sqrt[3]{\frac{m}{d_c}}}, \quad \text{or} \quad \frac{m\mu' \sqrt[3]{d_c}}{T_c} = \text{constant.} \quad (21)$$

This equation is tested for the substances under examination and the results of the test are shown in Table III. The data for the twenty-six substances shown were obtained from the excellent measurements by Young already cited. The approximate truth of equation 21 is abundantly confirmed, although the variations in the constant shown are considerably greater than can be attributed to the error of the measurements used.

TABLE III.

Substance.	$\frac{m}{T_c}$	$\mu' \sqrt[3]{d_c}$	$\frac{m\mu' \sqrt[3]{d_c}}{T_c}$ Equation 21.	$E_k$ Eq. 24.	C. Eq. 26.
Ethyl oxide .....	·1587	66·42	10·5	18·79	1·767
Di-isopropyl .....	·1721	60·70	10·4	17·33	1·751
Di-isobutyl .....	·2076	54·17	11·2	14·36	1·886
Isopentane .....	·1565	65·01	10·2	19·06	1·705
Normal pentane .....	·1534	67·58	10·4	19·45	1·737
„ hexane .....	·1696	63·39	10·7	17·58	1·803
„ heptane .....	·1854	60·79	11·3	16·08	1·890
„ octane .....	·2005	57·30	11·5	14·87	1·926
Hexamethylene.....	·1521	67·27	10·2	19·61	1·715
Benzene.....	·1390	73·49	10·2	21·45	1·713
Fluor-benzene .....	·1717	60·60	10·4	17·36	1·745
Chlor-benzene .....	·1780	58·38	10·4	16·75	1·743
Brom-benzene .....	·2344	43·59	10·2	12·72	1·713
Iodo-benzene.....	·2828	36·20	10·2	10·54	1·717
Carbon tetrachloride ...	·2765	36·22	10·0	10·78	1·680
Stannic chloride .....	·4407	24·00	10·6	6·76	1·775
Methyl formate .....	·1233	84·38	10·4	24·19	1·744
Ethyl formate .....	·1457	73·52	10·7	20·47	1·796
Methyl acetate .....	·1461	75·35	11·0	20·41	1·846
Propyl formate.....	·1637	66·81	10·9	18·21	1·834
Ethyl acetate .....	·1684	66·75	11·2	17·71	1·885
Methyl propionate .....	·1660	67·18	11·1	17·96	1·870
Propyl acetate .....	·1859	62·04	11·5	16·04	1·934
Ethyl propionate .....	·1870	61·07	11·4	15·95	1·914
Methyl butyrate .....	·1842	61·14	11·3	16·19	1·888
Methyl isobutyrate .....	·1889	59·29	11·2	15·79	1·877

The relations are, however, not so simple as the above argument would seem to indicate. For equation 21 can be immediately obtained by combining equation 1 and the relation of Dieterici,  $\lambda = CRT \ln \frac{d}{D}$ , and obtaining the limit of the resulting equation at the critical temperature. Thus we have, when  $v$  and  $V$  denote volumes of one gram of liquid and vapour respectively :

$$C = \frac{\mu'(\sqrt[3]{d} - \sqrt[3]{D})}{RT \ln V/v} = \frac{\mu'}{RT} \cdot \frac{V - v}{\ln V/v (Vv^{1/3} + V^{2/3}v^{2/3} + V^{1/3}v)}, \quad (22)$$

which at the critical temperature becomes

$$C = \frac{\mu' V_c}{3RT_c V_c^{4/3}} = \frac{\mu' \sqrt[3]{d_c}}{3RT_c} = \frac{m\mu' \sqrt[3]{d_c}}{3 \times 1.9861 T_c}. \quad (23)$$

Now the kinetic energy,  $E_k$ , of the molecules of one gram of a substance at the critical temperature is

$$E_k = 3/2 RT_c = 2.979 \frac{T}{m} \text{ calories,} \quad (24)$$

and the energy necessary to overcome the molecular attraction and cause the molecules to fly apart to an infinite distance is, from equation 1, since  $D=0$ ,

$$\lambda_{\infty} = \mu' \sqrt[3]{d_c} \text{ calories.} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Equation 23 may therefore be written :

$$C = \frac{\mu' \sqrt[3]{d_c}}{2E_k} = \frac{\text{energy necessary to overcome molecular attraction.}}{2 \times \text{kinetic energy of molecules}}. \quad . \quad . \quad . \quad . \quad (26)$$

I give the values of  $E_k$  obtained from equation 24 and of  $C$  as obtained from equation 26 in Table III. If the values of  $C$  there shown be compared with the average value of  $C$  for the substance in question as given in Table II. a satisfactory agreement will be noted.

I have cited these relations because they indicate some simple and deep-seated relation between the energy of molecular attraction and the temperature energy. I do not pretend to understand the significance of these relations clearly myself. But of this I feel sure, the fact that it is possible to distinguish and find a simple relation between the energy of molecular attraction and the kinetic (temperature) energy of the molecules at the critical temperature points to the correctness of the conclusion formerly reached, namely : *Change of temperature does not change the nature or the amount of the molecular attractive force. The temperature merely determines the orbit that the molecules will follow in obedience to the attractive force.*

Camden, S. C., U.S.A.,  
Dec. 9th, 1910.

## VI. *The Pianoforte Bridges.* By G. H. BERRY\*.

[Plate I.]

**I**N every pianoforte there are two bridges : one of which we may call the fixed bridge, which is the higher in the Upright pianoforte and nearer the key-board in the Grand ; and the other we may call the free bridge, which is glued and screwed direct to the sound-board in both types of instrument.

The fixed bridge is usually of metal and forms part of the framing of the pianoforte. It is practically rigid and not directly connected to the sound-board, and therefore plays

\* Communicated by Prof. E. H. Barton, D.Sc., F.R.S.E.

no part in communicating the vibrations of the string to the sound-board. It is used to determine the vibrating length of the string and the striking-point of the hammer.

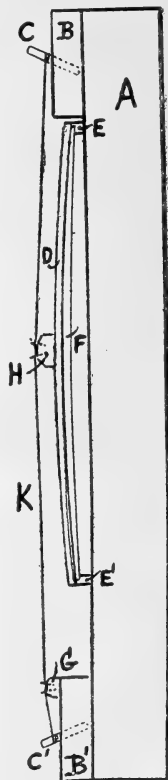
Some experiments with the other or free bridge are recorded in this paper.

The construction of the pianoforte may be illustrated by fig. 1. The iron frame is omitted for the sake of clearness. A is a heavy beam of wood, holding B, B', pieces of beech into which the tuning-pins C, C' are driven. D is the sound-board, supported by the fillets E, E'. The sound-bar F is glued to the back of the sound-board. G is the fixed and H the free bridge. The steel string K passes between two iron pins driven into the free bridge H: these pins are not parallel but dip towards one another, and hold the string on the bridge but do not prevent it from sliding over the face of the bridge when the string is being tuned. The part of the string between H and C is technically called the back-wire, and is permanently damped by a piece of baize. The vibrating length of string is that portion between G and H, and when struck with a pianoforte hammer it is forced towards the sound-board.

There are three different ways in which the vibration of the string may be transmitted to the sound-board through the free bridge.

(1) Any deflexion of the string will obviously cause a pull upon the free bridge H in a direction parallel to the string and towards the fixed bridge G. The movement of the bridge will be transmitted to the sound-board, deflecting it towards the back wire in the upper half and away from the string in the lower half. As the string comes back to its normal position the bridge and sound-board will also be allowed to return, but as the string swings out and away from the sound-board the bridge will again be subject to a pull parallel to the string, and the sound-board will be deflected in the same way as during the first movement of the string. In this way, the bridge and sound-board will have a frequency twice that of the string but, as the sound we hear comes from the sound-board and not

Fig. 1.



from the string, this is contrary to all experience, and a little consideration will show that the vibration of the string may be transmitted to the sound-board in two other ways.

(2) Suppose the bridge to be capable of a small movement in a direction parallel to the string and to have a frequency double that of the string; then it is possible to imagine the sound-board set in vibration by this movement of the bridge and to move towards the string on one downward motion of the bridge and away from the string on the second motion of the bridge, and thus the frequency of the sound-board would be in agreement with that of the string. (Melde's experiments with tuning-forks and strings will occur to the reader.) If the sound-board and string were flat, any such motion of the bridge would mean a corresponding extension of the material of the sound-board and back-wire, and, considering the high elasticity of pianoforte steel wire, whatever motion was possible would be exceedingly small. In practice, the sound-board is always curved like the belly of the violin and the string always passes at less than a right-angle over the edge of the free bridge. Leaving this movement of the bridge for the moment, let us consider the third way in which the sound-board may be set in vibration.

(3) The string, as it vibrates, not only has a tendency to pull the bridge down parallel to itself but it presses and pulls the bridge during each vibration in a direction at right-angles to the string, thus setting bridge and sound-board in vibration with a frequency the same as that of the string, and also the two halves of the sound-board will be in phase with one another.

A movement of the bridge and sound-board at right-angles to the string will increase or lower the tension in the back-wire, and when the tension is lowered will allow the bridge to move down slightly, parallel to the string, and in this way a vibration of the sound-board set up as in (2) above is made possible.

### *Experiments on Monochord.*

The following experiments were carried out on a monochord constructed as shown in fig. 1. The string used was 99 cm. long and was heavily spun with copper. It was taken from the last note on a pianoforte and was tuned to B<sub>11</sub> (31 vbps/sec.). The sound-board was 15 cm. wide, 0.7 cm. thick, and 86 cm. between the fillets. The sound-bar was 2.0 cm. thick and 2.16 cm. wide. The bridge was at the middle of the sound-board.

The resistance offered by the free bridge to a horizontal

and vertical deflexion was obtained in the following way :— A 6 lb. weight was attached to the middle of the string by a thin cord passing over a pulley and pulled the string towards the sound-board. The movement of the bridge was measured with a vernier microscope. Half the weight or 3 lbs. may be considered as acting on the free bridge. The observed mean deflexions of the free bridge were 0.060 cm. at right-angles to the string and 0.003 cm. parallel to the string. When a force is applied at the middle of the string and at right-angles to it, the corresponding movement of the free bridge is therefore 20 times greater in the direction at right-angles to the string, or horizontally, than it is vertically. It would therefore seem that the horizontal motion of the bridge setting the sound-board in vibration, as in (3), is likely to be much greater than the motion of the bridge parallel to the string and setting the sound-board in vibration as in (1) and (2).

#### *Photographic Curves.*

The next step was to obtain photographic time-displacement curves by means of the optical lever.

A beam of light from an electric arc passes through a narrow vertical slit and falls upon a small concave mirror mounted on a tiny three-legged table. One leg of the table is connected to the face of the bridge, and the other two rest in a hole and slot respectively on an independent support. The table is held in place by elastic bands. Any movement of the bridge at right-angles to the string causes the beam of light reflected by the mirror to vibrate horizontally. The image of the slit is focussed on a strip of photographic film fastened round the drum of an ordinary phonograph. A horizontal slit is fastened immediately in front of the film, this allows a small square of light only to fall on the film. In front of the film is also a 1/1 plate shutter with pneumatic release. To obtain the photograph of the vibrations of the bridge parallel to the string the optical lever is mounted with one leg attached to the lower side of the bridge, and the vibrations of the beam of light being then vertical, the drum of the phonograph and the two slits have to be arranged accordingly.

The distance of the leg of the optical lever attached to the bridge from the line joining the other two legs was 0.35 cm., and the distance between the mirror and the film was 127 cm. Thus the magnification would be 360.

The speed of the film was 67.7 cm. per second.

The string used was 99 cm. long between the bridges, was

heavily spun with copper, and tuned to  $B_{11}$  giving 31 vbns/sec. It was struck at  $\frac{1}{6}$  of its length from the fixed bridge by a pianoforte hammer. The force of the blow was made the same in all cases by a small weight being allowed to drop from a constant height on the key working the hammer. The exposure was made 3 seconds after the string was struck.

No. 1 Pl. I. shows the optical lever mounted to record the horizontal vibrations of the bridge.

No. 2 the same lever mounted to record the vertical vibrations. In both photographs L is the cross-bar carrying B a thick brass plate. Two legs of the optical lever T rest in a hole and slot respectively in the plate B. M is the mirror and S the straw. The latter, together with a small wooden base and a needle, acts as the third leg of the lever and forms the connexion with the bridge A. K is the sound-board. The three steel strings W were replaced in the experiment described by one steel string heavily spun with copper.

No. 3 shows the curve for the vibration of the bridge at right-angles to the string.

No. 4 shows the curve for the vertical vibration parallel to the string.

The amplitude of No. 1 is about 5.3 times as great as that of No. 2. Although considerably greater the difference is not so much as the experiment with the weights described above would lead us to suppose. It will be noticed that the octave is prominent in No. 3, and in No. 4 we get only the octave as we should expect.

Returning to the consideration of the vibration of the sound-board as set up in the manner described in (1), we saw that the bridge acting as a lever upon the sound-board would set the latter in vibration with its two halves in opposite phase.

The optical lever gives us a means of testing this. Two levers were set up one on each side of the free bridge and about 7.5 cm. distant from it. A mirror on each lever threw images of the slit on the film, and a simultaneous photograph of the vibrations at these two points on the sound-board were thus obtained.

Nos. 5 and 6 show this. Three steel strings, No. 18 gauge, 137 cm. long and tuned to  $A\sharp 116$ , were used. It will be seen that the phase of the two is the same, and this shows that the sound-board is not set in vibration as described in (1).

#### *Soundless Vibrations of a String.*

An interesting little experiment which may be performed on any pianoforte may be here described. Place on the

lowest key of the instrument a small weight sufficient to keep the damper off the string. Then set this string vibrating by plucking it with the fingers. The sound thus produced will last about 10 or 15 seconds, but the string will continue to vibrate for another 30 seconds or longer, and during the latter part of the time no sound will be audible.

The string vibrates in two planes: one parallel to the surface of the sound-board, and the other at right-angles to it. We have seen that the vibration of the string is transmitted to the sound-board most effectively by the pressing and pulling of the string on the bridge at right-angles to the surface of the sound-board. The vibration of the string in this plane is rapidly absorbed by the sound-board and therefore the audible sound rapidly ceases, but the vibration parallel to the surface of the sound-board does not set the latter in vibration to any appreciable extent, and therefore the vibration in this plane continues a much longer time and no sound is heard. By sliding a straight-edge along the face of the adjoining strings and gradually bringing it over the vibrating string, it will be found that the latter will hardly touch the straight-edge, thus showing the vibration to be in one plane.

14 City Road, London, E.C.  
March 23, 1911.

## VII. *Elliptic and other Interference with Reflecting Gratings.*

By C. BARUS, Ph.D., LL.D., Professor of Physics at Brown University, Providence, U.S.A.\*

1. **FIRST METHOD.**—There are two or three typical cases in the use of reflecting gratings for the production of interferences in the spectrum, each of which shows peculiarly interesting features. The first of these is given in fig. 1, and corresponds closely to the method described for transmission gratings in a preceding paper †. If L is the source of light and M a glass plate grating, it was shown that plane mirrors in the positions  $G_m$  and  $G_n$ , each reflecting a spectrum from M, produce elliptical interference whenever the rays returned after passing M by transmission and reflexion, respectively, are made to overlap in the spectrum, under suitable conditions.

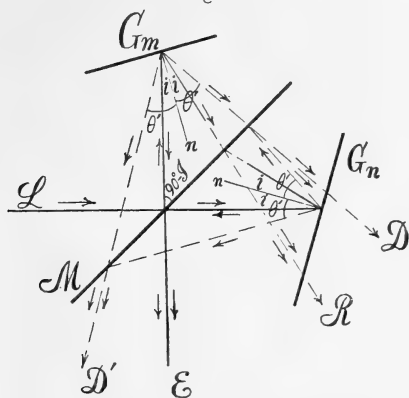
\* Communicated by the Author. Abridged from a Report to the Carnegie Institution of Washington, D.C. Cf. Note in 'Science,' January 20, 1911.

† Phil. Mag. July 1910.



The present method is the converse of this, since the gratings and the opaque mirrors change places. Parallel rays from *L* strike the plate of glass *M* and the component

Fig. 1.



rays reach identical reflecting gratings  $G_m$  and  $G_n$ , placed symmetrically with respect to *M* at an angle  $i$  to the *E* and *L* directions. The undeviated rays pass off eccentrically at *R* and are not seen in the telescope at *E*. They may, however, be seen in an auxiliary telescope pointed in the line *R*, and they then facilitate the adjustments. Rays diffracted at the angle  $2i$ , however, are respectively transmitted and reflected by *M* and interfere in the telescope in the line *E*. Similarly rays diffracted at an angle  $\theta' > i$  interfere in the line *D*.

To make the adjustment it is sufficient to bring the Fraunhofer lines in the two spectra seen at *E* into complete coincidence, horizontally and vertically. Coincidence of slit images at *R* (at least vertically) aids in the same result. It is also necessary that the rulings on  $G_m$  and  $G_n$  and the slit should be parallel, or that the images of slit and spectra shall lie between the same horizontals in the field. One of the gratings,  $G_n$ , may now be moved parallel to itself by the micrometer screw until the elliptic interferences appear. If the plate *M* is not half silvered there are three groups of these, as described in the preceding paper. Each group passes from the initial degree of extreme fineness, through maximum size, to a final degree, for a play of the screw of about 1 mm. There is the usual radial motion of the fringes, together with the drift through the spectrum as a whole. To bring out the set of solitary ellipses, the silvered surface of *M* should be towards the light and remote from the eye.

As a rule the adjustment is difficult, as an extra condition is imposed in the parallelism of the slit and the rulings of the gratings. The ellipses are liable to be coarse with their axes oblique, clearer in some parts of the spectrum than in others, unless means are provided for placing the rulings accurately parallel. Even when well adjusted they are rather polygonal than rounded in their contours. They are about as strong with non-silvered glass M as with half-silvered glass; but in view of the multiple spectra, the adjustment is much more difficult in the former case.

It has been suggested that the white slit images must appear eccentrically in the direction R. Hence, if a special telescope is directed in this line, the final adjustment is reached on coincidence of the proper slit images, provided the rulings of the gratings and the slit are parallel.

For  $\theta' > i$  the second series of interference spectra occurring at D eccentrically are broader, but only on perfect adjustment do they occur simultaneously with the other set. In fact, since for the preceding case  $i = \theta$ , or

$$2 \sin i = \lambda/D,$$

and in the present case

$$\sin \theta' - \sin i = \lambda/D,$$

therefore

$$\sin \theta' = 3 \sin i = 3 \sin \theta.$$

There is also an available set in the second order to the left of E. In the gratings used above, D lies in front of  $G_n$ , being nearer the E than the L direction.

2. *Inversion of the Method.*—The occurrence of the undeviated ray R suggests another method. For if the white ray R is *reversed*, i. e. comes from an eccentric collimator, slit images will be seen in telescopes at L and E, whereas overlapping spectra will appear in the direction D' eccentrically and in the lines R and R'. One of the latter may be lost in the collimator. The former occurs for the same angle  $\theta'$ , so that

$$\sin \theta' = 3 \sin i.$$

Moreover, if  $I = 45^\circ$  is the angle of incidence of L upon M when sodium light is taken, so that

$$\theta' = 26^\circ 14', \quad i = 8^\circ 28',$$

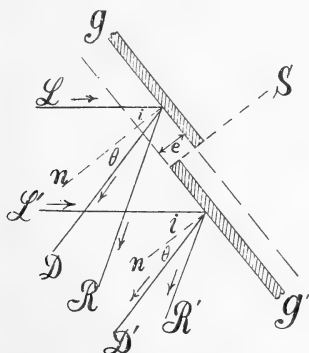
the R, D, D' rays make angles  $2i$ ,  $\theta' + i$ ,  $\theta' - i$ , respectively, with the E direction; or the sum of the angles at D and D'

with the E line is  $2\theta'$ , their difference  $2i$ , and the rays D, R, D' intersect at a common centre on  $G_m$ . Hence, if we place the plane of  $G_m$  at the centre of the spectrometer and arrange M and  $G_n$  eccentrically, the angles may be measured as before.

3. *Resolution of the Slit Image.*—If the sharp white images of the slit in a Michelson apparatus for the case in which the incident light consists of parallel white rays from a collimator, be accurately superimposed, and the opaque mirrors be set at the proper distances from the semi-transparent mirror by the micrometer, the slit image may itself be viewed through a grating and will then show elliptic interferences in all the spectra. The apparatus is here eccentric, while the grating (either transmitting or reflecting) must be at the centre of the spectrometer, if angles are to be measured. The same is true for any of the other superimposed white slit images in the above or the earlier experiments, and may even be repeated with successive transmitting gratings. It is interesting to note that the position of the centre of ellipses is at the same wave-length in all the spectra, though the form of ellipses may differ enormously. The same phenomenon may thus be seen by a number of observers at the same time, each looking through his own telescope.

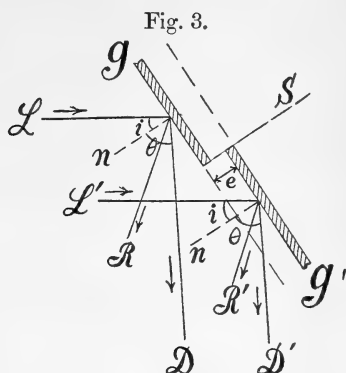
4. *Third Method. Parallel Gratings.*—In this case the two halves of the grating treated are displaced parallel to themselves, from their original co-planar position in the grating, from which they are cut. Their mounting is thus something like the case of the two black plates of Fresnel's mirror apparatus, one of the plates being adapted for displacement parallel to itself.

Fig. 2.



In fig. 2,  $g$  and  $g'$  show the two halves of the reflecting grating, cut along the plane  $S$ , normal to the plates and

parallel to the rulings. The half  $g'$  is provided with a micrometer screw, so that it may be successively moved from the position  $g'$  in fig. 2 to the position  $g'$  in fig. 3, through all



intermediate positions, while the half  $g$  remains stationary. Each of the halves  $g$  and  $g'$  is controlled by three adjustment screws (horizontal and vertical axes of rotation), to secure complete parallelism of the faces of the grating. Each, moreover, may be rotated around a horizontal axis to place the lines parallel to the slit of the collimator. The duplex grating is mounted on a spectrometer as is usual for reflexion. Finally, each half may be raised and lowered and moved horizontally to and fro, parallel to itself, so that the half gratings when coplanar may approximately reproduce the original grating.

After each of the spectra is clear as to Fraunhofer lines, the interferences here in question are produced by bringing these lines (the D lines for instance) into perfect coincidence, horizontally and vertically. Under these circumstances if the distance apart,  $e$ , is suitably chosen, the interference fringes will appear throughout the spectrum. These consist of an approximately equidistant series of lines parallel to the slit, *i. e.* vertical lines, which are finer, *cet. par.*, as the breadth of the crack at  $S$  between the gratings is larger. They may be increased from the extreme fineness as they enter the range of visibility, to a maximum coarseness (in the above experiments) of about 3 to 5 minutes of arc per fringe, after which they vanish. They cannot in practice be passed through infinite size; neither can they be produced symmetrically on the two sides of the adjustment for infinite size. They cannot, in other words, be changed from the positive to the negative condition of appearance.

The occurrences are in fact as follows: if, as in fig. 2,  $i > \theta$  (parallel white rays coming from L and L', R and R' being reflected, D and D' diffracted rays for the normal  $n$ ), the grating  $g'$  must be in advance or forward of  $g$ . If now the airspace  $e$  is reduced micrometrically,  $g'$  retreating, the lines travel in a given direction (from left to right) through the spectrum, while at the same time they grow continually larger until for a minimum value of  $e$  still positive, they *vanish as a whole*. The period of indistinctness before evanescence is not marked.

On the other hand, if  $\theta' > i$ , as in fig. 3, the grating  $g'$  must be to the rear of  $g$  and the airspace  $e$  is throughout negative. If this is now decreased numerically the lines travel through the spectrum in the opposite direction to the preceding case, while at the same time they coarsen until they vanish as a whole, as before. The grating  $g'$  is still behind  $g$  when this occurs.

Finally, if for any suitable value of  $e$  the grating  $g'$  is moved in its own plane without rotation away from  $g$ , so as to widen the crack at S between them, the fringes grow continually finer until they pass beyond visibility, and *vice versa*; i. e., as the crack at S is made smaller the lines continually coarsen.

5. *Nature of the Evanescence.*—The fact that the lines vanish as a whole and almost suddenly after reaching their maximum distance apart is very peculiar, as is also the fact that they cannot be passed through infinite size or appear symmetrically on both sides of this adjustment. To investigate this case I provided both the collimator and the telescope with slits so that the parts of the grating  $g$  and  $g'$  from which the interfering pencils come might be investigated.

If a single vertical slit about 1 mm. wide is passed from right to left towards the objective of the telescope, a black line passes across the field of the spectrum, which line is merely the image of the crack at S. Let the green rays, for instance, come from the edge of both gratings  $g$  and  $g'$ , whereas the red rays and the violet rays come from but a single grating. Now when the space  $e$  is diminished, the black band in the green gradually vanishes, and in its place appear the coarsest fringes producible. When the slit F is removed these coarse fringes disappear. The fringes visible through the slit have, however, both an inferior and superior limit in  $e$  and in angular size. When  $e$  is diminished to zero they vanish and when  $e$  is sufficiently increased they again vanish, though they now appear when the slit is either removed or widened. From this it follows that the coarsest

fringes come from the edges of the crack S of the gratings, and that the remainder of the grating will not produce coarse fringes. By moving the slit the fringes may be made to appear in any other part of the spectrum.

The same fact may be proved by putting a vertical slit over the lens of the collimator and allowing white light to fall on the edges of the grating at S. Coarse fringes limited as to range and size are then seen throughout the spectrum.

Whenever the slit or vertical stop is used, the fringes are exceptionally sharp and easily controlled for micrometry. It is not even necessary to adjust the two spectra horizontally with the same care as when no slit is used; but the vertical coincidence of spectrum lines must be sharp. Naturally the use of the slit has one drawback, as the resolving power of the grating is decreased and the spectrum lines are only just visible. The adjustment, however, may be made before the slit is added. A few examples may be given: For a slit 1 mm. wide over the telescope or collimator, only the immediate edges at the crack S, about  $1/2$  mm. each in breadth, are active. A narrow range of large fringes is seen in the field easily controlled by the micrometer screw. With a slit 3 mm. in width the lower limit is much increased, the upper diminished, to a size of about  $3'$  of arc per fringe. In the absence of the slit the field is free from fringes. With a slit 6 mm. wide, the upper limit is again decreased, the lower much increased; nevertheless the finest fringes appear only after the slit is removed. Using double slits over the collimator, each 1 mm. wide and 3 mm. apart, fringes of medium size limited at both ends appear; 3 mm. slits 6 mm. apart show only the very fine fringes, but both sizes are still limited. Finally, when all but about  $1/2$  mm. of the edge of the crack of the grating  $g'$  is screened off, whereas the whole grating  $g$  (about  $1/2$  inch square) is without a screen, all the fringes from the maximum size to complete evanescence beyond the range of visibility are producible. Naturally if the edge of  $g'$  is quite dark everything vanishes.

It follows, therefore, that pairs of corresponding rays are always in question. These corresponding rays are at a definite distance,  $ND$ , apart, where  $D$  is the grating space and  $N$  the number of lines per centim. of the grating in question. This distance  $ND$  is greater as the fringes are smaller, and may be of the order of a centimetre when the fringes pass beyond the range of visibility. Again,  $ND$  is equal to the width of the crack when the largest fringes

vanish. Finally, when  $ND$  is zero, as in the original unbroken grating, the size of the fringes is infinite.

It has been stated that the use of the slit or a laterally limited objective is advantageous because all the lines are much sharper. Inert or harmful illumination is cut off. If the slit is over the objective of the telescope only a small part of the field of view shows the lines; if placed over the objective of the collimator, the fringes are of extreme clearness throughout the spectrum. It may be ultimately of advantage to use the edge near the crack  $g'$  only, together with the whole of  $g$ . For if a small strip of  $g'$  at the crack  $S$  is used with the whole of  $g$ , the smaller fringes are weakened or wiped out. Thus the inner edge of the nearer grating with successive parts of the further grating is chiefly effective in the production of these interferences.

To bring the two edges quite together was not possible in my work, as they were rough and the apparatus improvised.

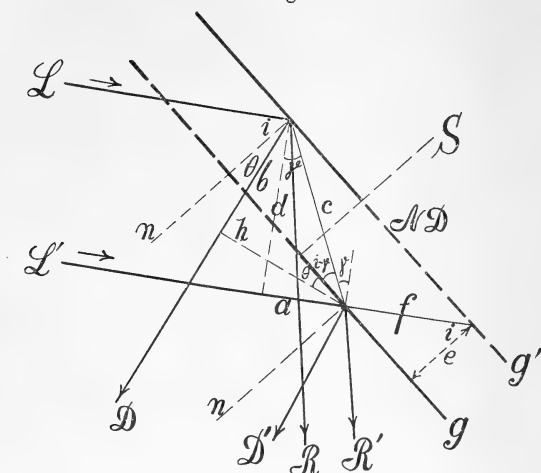
7. *Data.*—Some measurements were attempted, with the view only of checking the equations presently to be deduced. The adjustment on an ordinary spectrometer is not firm enough, and the fringes being very fine (a few minutes of arc) are difficult to follow unless quite stationary.

These observations gave both the values of  $de/dn$ , displacement per fringe, for different angles of incidence  $i$  and of diffraction  $\theta$ , and  $d\theta/dn$ , the angular deviation per fringe at the  $D$  line. In measuring the latter it was necessary to count the fringes between the  $C$  and  $D$  lines and divide their angular distance apart by these numbers. As  $e$  cannot be measured, its successive increments  $\Delta e$  from the first position must be used. These are presently to be associated with the corresponding increments of  $dn/d\theta$ . The data will be found in the original paper.

8. *Equations.*—In fig. 4 (p. 126),  $L$  and  $L'$  represent a pair of corresponding white rays, reflected into  $R$  and  $R'$  and diffracted into  $D$  and  $D'$  at angles  $i$  and  $\theta$ , respectively. The half gratings  $g$  and  $g'$  are separated along the crack  $S$ , and  $g'$  is movable parallel to itself by a micrometer screw normal to  $g'$ . Let the normal distance apart of the gratings be  $e$ . The incident rays  $L$ ,  $L'$  strike the originally coplanar grating at points  $N$  rulings apart, or  $ND$  cm. apart, if  $D$  is the grating space. In the separated grating let these points be at a distance  $c$  apart. Let  $d$  be the incident wave front and  $h$  the corresponding diffracted wave front, and call the angle between  $c$  and  $d$ ,  $\gamma$ .

When there is reinforcement the path difference of the rays  $L$  and  $L'$  from the incident ( $d$ ) to the diffracted ( $h$ )

Fig. 4.



wave front, may be written

$$n\lambda = b - a,$$

where  $b$  and  $a$  are the distances of  $h$  and  $d$  from the points of incidence of  $L$  and  $L'$  on the gratings  $g$  and  $g'$ , respectively. If, finally,  $f$  is the length of the prolongation of  $L'$  between the gratings we may write in succession

$$d = ND \cos i, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$f = e \sec i, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$a = ND \sin i - e \sec i, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\tan \gamma = a/d, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$c = ND \cos i \sec \gamma, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$b = c \sin (i + \theta - \gamma) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

To these should be added

$$dN/de = \tan i/D. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence, after removing  $\gamma$ , arranging and reducing,

$$n\lambda = ND (\sin \theta - \sin i) + e \sec i (1 + \cos (i + \theta));$$

or since  $\sin i - \sin \theta = \lambda/D$ ,

finally,

$$(n + N)\lambda = e \frac{1 + \cos (i + \theta)}{\cos i} = \frac{2e \cos^2 (i + \theta)/2}{\cos i}. \quad . \quad . \quad (8)$$



This must, therefore, be regarded as the equation of the phenomenon. Equation (7) however leads on integration to

$$N = e \tan i/D + N_0, \quad . \quad . \quad . \quad (9)$$

where  $N_0 D$  is the width of the crack.

If the value of  $N$  from (9) is put into (8) together with the equivalent of  $\lambda/D$ , it appears after reduction that

$$(n + N_0) \lambda = e (\cos i + \cos \theta) = 2e \cos \frac{i + \theta}{2} \cos \frac{i - \theta}{2}.$$

The case of  $N = 0$ ,  $e > 0$  would correspond to the equation

$$n\lambda = e (1 + \cos (i + \theta)) / \cos i, \quad . \quad . \quad . \quad (10)$$

which is only a part of the complete equation (8). In the case of  $i > \theta$ , one active half is necessarily partly behind the other half, and therefore not adapted to bring out the phenomenon as explained, unless  $e = 0$ .

9. *Differential Equations.* *Displacement per fringe,  $de/dn$ .*—To test equations (8) or (10) increments must be compared. The latter gives at once, since  $N$  is constant relative to  $e$ , like  $i$ ,  $\theta$ , and  $\lambda$ ,

$$\frac{de}{dn} = \frac{\lambda}{\cos i + \cos \theta} = \frac{\lambda}{2 \cos \frac{i + \theta}{2} \cos \frac{i - \theta}{2}}, \quad . \quad . \quad (11)$$

which is the interferometer equation when the fringes pass a given spectrum line, like either D line, which is sharp and stationary in the field. Equations (7) and (11), moreover, give after reduction

$$dN/dn = \tan i \tan \frac{i - \theta}{2}. \quad . \quad . \quad . \quad (12)$$

Values of  $de/dn$  computed from (11) agreed as well with observations made under widely different conditions ( $i > \theta$ ,  $i < \theta$ , first and second order), as the small fringes and the difficulty of getting the grating normal to the micrometer screw in my improvised apparatus, admit. If this adjustment is not perfect  $N_0$  changes with  $e$ . From equation (12) moreover,

$$\frac{dN}{dn} = \frac{dN}{d\theta} \frac{d\theta}{dn} = \frac{dN_0}{d\theta} \frac{d\theta}{dn} = \frac{dN_0}{dn}, \quad . \quad . \quad . \quad (12')$$

since  $N_0$  is constant only relative to  $e$  when  $\theta$  varies.

10. *Deviation per Fringe, &c.,  $d\theta/dn$ ,  $d\theta/de$ .*—These measurements are still more difficult in the absence of special apparatus, since  $e$  is not determinable and the counting of fine flickering fringes is unsatisfactory; but the order of

results may be corroborated by observing the number of fringes between two Fraunhofer lines, like the C, D and other lines used. Differentiating equations (8) and (10) for variable  $n$ ,  $\lambda$ ,  $\theta$ , and  $N$  (since  $dN/d\theta$  is equal to  $dN_0/d\theta$ , equation 12'), and inserting  $-D \cos \theta \cdot d\theta/dn = d\lambda/dn$ , it follows, after arranging, that

$$\frac{d\theta}{dn} = \frac{\lambda^2}{eD} \frac{1 + dN/dn}{1 + \cos(i + \theta)} = \frac{\lambda}{e \cos i} \tan \frac{i - \theta}{2}. \quad (13)$$

Combining this with (11),

$$\frac{d\theta}{dn} = \frac{\lambda}{eD \cos i} = \frac{\sin i - \sin \theta}{e \cos i}. \quad (14)$$

Since in equation (13),  $e$  is not determinable it is necessary to compare increments  $\Delta dn/d\theta$  in terms of the corresponding increments  $\Delta e$ , whence

$$\Delta(dn/d\theta) = \left( \cos i / \lambda \tan \frac{i - \theta}{2} \right) \Delta e. \quad (15)$$

My observations contain data of this kind, computed separately for the Fraunhofer lines D, C, &c., employed and their mean values. To find the mean width of fringes between these lines, their angular deviations were divided by the number of fringes counted between them at different values of  $e$ . The results agree as closely as the difficulty of the observations warrants. One may note that without removing  $N$ , the corresponding coefficients would be

$$\Delta d(n + N)/d\theta,$$

and these are found to be much more in error, here and in the preceding cases. If from  $d\theta/dn$ ,  $e$  is eliminated in terms of  $(n + N)$  the equation is

$$\frac{d\theta}{dn} = \frac{\lambda}{D} \frac{1}{(n + N_0) \cos i}, \quad (16)$$

so that for a given value of  $i$ ,  $\theta$ ,  $N_0$ , they decrease in size with  $n$ . If  $n=0$  they reach the limiting size

$$\frac{d\theta}{dn} = \frac{\lambda}{DN_0 \cos i}.$$

If the crack  $N_0D$  should be made infinitely small, they would be infinitely large. To pass through infinity,  $N_0$  must be negative, which has no meaning for  $i > \theta$  or would place one effective edge of the crack  $S$  behind the other. These inferences agree with the observations as above detailed. If, however,  $i < \theta$ , a negative value of  $N_0$  restores equation (16)

for  $n=0$  to equation (17), as was actually observed (figs. 2 and 3).

Finally, equation (14) might be used for observation in the incremented form

$$\Delta (de/d\theta) = \frac{D \cos i}{\lambda} \Delta e; \quad . \quad . \quad . \quad (17)$$

but I did not succeed with it. One loses track of the run of a fringe with  $de$ .

11. *Coloured Slit Images and Disk Colours of Coronas.*—In the above experiment the fringes were but a few minutes apart. It is obvious, however, that if  $N_0$  is sufficiently small the fringes will grow with decreasing  $n$ , in angular magnitude, until there are but a few black bands in the spectrum. Under these circumstances the undeviated image of the superimposed slits must appear *coloured*, particularly so, if an effect equivalent to  $N_0$  is present throughout the grating. This phenomenon of coloured slits is apparently of interest in its bearing on the theory of coronas, where there is also an interference phenomenon superimposed upon a diffraction phenomenon, as is evidenced by the brilliant disk colours. For instance, suppose a corona were produced by a sufficient number of fog particles distributed throughout a plane normal to the undeviated rays. Now let the alternate particles be moved *in the same way* slightly to the rear of their original position, and let the distance between the two planes be small relatively to the wave-length of light. In such a case there should be two identical coronas superimposed in all their parts, and they should therefore interfere. Inasmuch, however, as even small fog particles are of the order of size of  $\cdot 0001$  cm. and their mean distance apart 50 times larger, *i. e.*  $\cdot 005$  cm., it remains to be proved whether such an effect can be looked to as an explanation of the disk colours of coronas.

The phenomena of § 4 must be producible with a transmission grating, separated parallel to the rulings, with one component grating movable micrometrically, though I have not yet tested this case. Obviously it will only be interesting if obtainable from film gratings.

In this connexion I may state, in conclusion, that I have since succeeded in producing the elliptic interferences discussed in my last paper (*l. c.*), with such gratings, almost as brilliantly as with gratings ruled on glass. The film for this purpose is cemented, under pressure, with chloroformed Canada balsam, between unequal thicknesses of plate glass.

My thanks are due to Prof. A. A. Michelson, of the University of Chicago, for the loan of one of his reflexion gratings, with which the above results were tested.

VIII. *Aberration in a Dispersive Medium.*

By Lord RAYLEIGH, O.M., F.R.S.\*

THE application of the theory of group-velocity to the case of light was discussed in an early paper † in connexion with some experimental results announced by Young and Forbes ‡. It is now, I believe, generally agreed that, whether the method be that of the toothed wheel or of the revolving mirror, what is determined by the experiment is not  $V$ , the wave-velocity, but  $U$ , the group-velocity, where

$$U = d(kV)/dk,$$

$k$  being inversely as the wave-length. In a dispersive medium  $V$  and  $U$  are different.

I proceeded :—"The evidence of the terrestrial methods relating exclusively to  $U$ , we turn to consider the astronomical methods. Of these there are two, depending respectively upon aberration and upon the eclipses of Jupiter's satellites. The latter evidently gives  $U$ . The former does not depend upon observing the propagation of a peculiarity impressed upon a train of waves, and therefore has no relation to  $U$ . If we accept the usual theory of aberration as satisfactory, the result of a comparison between the coefficient found by observation and the solar parallax is  $V$ —the wave-velocity."

The above assertion that stellar aberration gives  $V$  rather than  $U$  has recently been called in question by Ehrenfest §, and with good reason. He shows that the circumstances do not differ materially from those of the toothed wheel in Fizeau's method. The argument that he employs bears, indeed, close affinity with the method used by me in a later paper ||. "The explanation of stellar aberration, as usually given, proceeds rather upon the basis of the corpuscular than of the wave-theory. In order to adapt it to the principles of the latter theory, Fresnel found it necessary to follow Young in assuming that the æther in any vacuous space connected with the earth (and therefore practically in the atmosphere) is undisturbed by the earth's motion of 19 miles per second. Consider, for simplicity, the case in which the direction of the star

\* Communicated by the Author.

† Nature, vols. xxiv., xxv., 1881; Scientific Papers, i. p. 537.

‡ These observers concluded that blue light travels *in vacuo* 1·8 per cent. faster than red light.

§ Ann. d. Physik, Bd. xxxiii. p. 1571 (1910).

|| Nature, vol. xlv. p. 499 (1892); Scientific Papers, iii. p. 542.

is at right angles to that of the earth's motion, and replace the telescope, which would be used in practice, by a pair of perforated screens, on which the light falls perpendicularly. We may further imagine the luminous disturbance to consist of a single plane pulse. When this reaches the anterior screen, so much of it as coincides with the momentary position of the aperture is transmitted, and the remainder is stopped. The part transmitted proceeds upon its course through the æther independently of the motion of the screens. In order, therefore, that the pulse may be transmitted by the aperture in the posterior screen, it is evident that the line joining the centres of the apertures must not be perpendicular to the screens and to the wave-front, as would be necessary in the case of rest. For, in consequence of the motion of the posterior screen in its own plane, the aperture will be carried forward during the time of passage of the light. By the amount of this motion the second aperture must be drawn backwards, in order that it may be in the place required when the light reaches it. If the velocity of light be  $V$ , and that of the earth be  $v$ , the line of apertures giving the apparent direction of the star must be directed forwards through an angle equal to  $v/V$ ."

If the medium between the screens is dispersive, the question arises in what sense the velocity of light is to be taken. Evidently in the sense of the group-velocity; so that, in the previous notation, the aberration angle is  $v/U$ . But to make the argument completely satisfactory, it is necessary in this case to abandon the extreme supposition of a single pulse, replacing it by a group of waves of approximately given wave-length.

While there can remain no doubt but that Ehrenfest is justified in his criticism, it does not quite appear from the above how my original argument is met. There is indeed a peculiarity imposed upon the regular wave-motion constituting homogeneous light, but it would seem to be one imposed for the purposes of the argument rather than inherent in the nature of the case. The following analytical solution, though it does not relate directly to the case of a simply perforated screen, throws some light upon this question.

Let us suppose that homogeneous plane waves are incident upon a "screen" at  $z=0$ , and that the effect of the screen is to introduce a reduction of the amplitude of vibration in a ratio which is slowly periodic both with respect to the time and to a coordinate  $x$  measured in the plane of the

screen, represented by the factor  $\cos m(vt-x)$ . Thus, when  $t=0$ , there is no effect when  $x=0$ , or a multiple of  $2\pi$ ; but when  $x$  is an odd multiple of  $\pi$ , there is a reversal of sign, equivalent to a change of phase of half a period. And the places where these particular effects occur travel along the screen with a velocity  $v$  which is supposed to be small relatively to that of light. In the absence of the screen the luminous vibration is represented by

$$\phi = \cos (nt-kz), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or at the place of the screen, where  $z=0$ , by

$$\phi = \cos nt \quad \text{simply.}$$

In accordance with the suppositions already made, the vibration just behind the screen will be

$$\begin{aligned} \phi &= \cos m(vt-x) \cdot \cos nt \\ &= \frac{1}{2} \cos \{(n+mv)t-mx\} + \frac{1}{2} \cos \{(n-mv)t+mx\}; \end{aligned} \quad (2)$$

and the question is to find what form  $\phi$  will take at a finite distance  $z$  behind the screen.

It is not difficult to see that for this purpose we have only to introduce terms proportional to  $z$  into the arguments of the cosines. Thus, if we write

$$\begin{aligned} \phi &= \frac{1}{2} \cos \{(n+mv)t-mx-\mu_1 z\} \\ &\quad + \frac{1}{2} \cos \{(n-mv)t+mx-\mu_2 z\}, \end{aligned} \quad (3)$$

we may determine  $\mu_1, \mu_2$  so as to satisfy in each case the general differential equation of propagation, viz.

$$\frac{d^2\phi}{dt^2} = V^2 \left( \frac{d^2\phi}{dx^2} + \frac{d^2\phi}{dz^2} \right). \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In (4)  $V$  is constant when the medium is non-dispersive; but in the contrary case  $V$  must be given different values, say  $V_1$  and  $V_2$ , when the coefficient of  $t$  is  $n+mv$  or  $n-mv$ . Thus

$$\left. \begin{aligned} (n+mv)^2 &= V_1^2(m^2+\mu_1^2) \\ (n-mv)^2 &= V_2^2(m^2+\mu_2^2) \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (5)$$

The coefficients  $\mu_1, \mu_2$  being determined in accordance with (5), the value of  $\phi$  in (3) satisfies all the requirements of the problem. It may also be written

$$\phi = \cos \{mvt-mx-\frac{1}{2}(\mu_1-\mu_2)z\} \cdot \cos \{nt-\frac{1}{2}(\mu_1+\mu_2)z\}, \quad (6)$$

of which the first factor, varying slowly with  $t$ , may be regarded as the amplitude of the luminous vibration.

The condition of constant amplitude at a given time is that  $mx + \frac{1}{2}(\mu_1 - \mu_2)z$  shall remain unchanged. Thus the amplitude which is to be found at  $x=0$  on the screen prevails also behind the screen along the line

$$-x/z = \frac{1}{2}(\mu_1 - \mu_2)/m, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

so that (7) may be regarded as the angle of aberration due to  $v$ . It remains to express this angle by means of (5) in terms of the fundamental data.

When  $m$  is zero, the value of  $\mu$  is  $n/V$ ; and this is true approximately when  $m$  is small. Thus, from (5),

$$\mu_1 - \mu_2 = \frac{\mu_1^2 - \mu_2^2}{2n/V} = \frac{2mv}{V} + \frac{nV}{2} \left( \frac{1}{V_1^2} - \frac{1}{V_2^2} \right)$$

and

$$\frac{\mu_1 - \mu_2}{2m} = \frac{v}{V} \left\{ 1 + \frac{n}{2mv} \frac{V_2 - V_1}{V} \right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

with sufficient approximation.

Now in (8) the difference  $V_2 - V_1$  corresponds to a change in the coefficient of  $t$  from  $n + mv$  to  $n - mv$ . Hence, denoting the general coefficient of  $t$  by  $\sigma$ , of which  $V$  is a function, we have

$$V_1 - V_2 = 2mv \cdot dV/d\sigma,$$

and (8) may be written

$$\frac{\mu_1 - \mu_2}{2m} = \frac{v}{V} \left\{ 1 - \frac{\sigma}{V} \frac{dV}{d\sigma} \right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Again,

$$V = \sigma/k, \quad U = d\sigma/dk,$$

and thus

$$\frac{\sigma}{V} \frac{dV}{d\sigma} = k \frac{dV}{d\sigma} = 1 - \frac{\sigma}{k} \frac{dk}{d\sigma},$$

and

$$1 - \frac{\sigma}{V} \frac{dV}{d\sigma} = \frac{\sigma}{k} \frac{dk}{d\sigma} = \frac{V}{U},$$

where  $U$  is the group-velocity.

Accordingly,

$$-x/z = v/U \quad . \quad . \quad . \quad . \quad . \quad (10)$$

expresses the aberration angle, as was to be expected. In the present problem the peculiarity impressed is not

uniform over the wave-front, as may be supposed in discussing the effect of the toothed wheel; but it exists nevertheless, and it involves for its expression the introduction of more than one frequency, from which circumstance the group-velocity takes its origin.

A development of the present method would probably permit the solution of the problem of a series of equidistant moving apertures, or a single moving aperture. Doubtless in all cases the aberration angle would assume the value  $v/U$ .

Terling Place, Witham,  
May 19, 1911.

IX. *On a Method of Investigating the Quantity of Radium in Rocks and Minerals, &c.* By J. JOLY, F.R.S.\*

THE method commonly in use for investigating the radium content of rocks and minerals leaves much to be desired. The rock is first treated chemically so as to bring it into solution. Generally this is effected by fusion with alkaline carbonates. Leaching, filtration, and acidification follow; the rock substance being finally obtained in two bulky solutions: an alkaline, resulting from the leaching of the melt, and an acid, resulting from the solution in acid of the insoluble residue. It is difficult to obtain quite limpid acid solutions; several filtrations and successive fusions with carbonates have often to be resorted to; and it not infrequently happens that even then a solution of perfect limpidity cannot be obtained. A trace of precipitate may involve the imperfect solution of the radium; and the complete liberation of the emanation by ebullition may be, subsequently, impossible. This may, in some cases, be demonstrated by adding to the acid solution a trace of sulphuric acid, when it will be found that if any precipitate is formed a fractional part only of the emanation can be subsequently boiled off. By treating a solution of a tinguaitite in this manner, Eve and McIntosh (*Phil. Mag.* Aug. 1907) found that only one-fifth of the amount of emanation originally obtained could be removed by boiling. I have found that a trace of barium added to the rock solution along with sulphuric acid, will bring about this result. So also Levin (*Phys. Zeit.* xi. 1910, p. 323) found that by adding some  $\text{BaCl}_2$  and  $\text{H}_2\text{SO}_4$  to mineral waters less than one per cent. of the radium remained unprecipitated as judged by the emanation.

\* Communicated by the Author.



The causes which retain emanation in certain solutions appear to be obscure. Rock solutions may occasionally yield diminished, occasionally increased, amounts of emanation on successive experiments. These cases seem to be exceptional. There is some reason to believe that, additional to that part of the emanation which is soluble in the boiling solution, emanation may be retained from some other cause or causes. This has been referred to as explained by adsorption. This explanation may apply to the case of perfectly limpid solutions containing radium, and from which only a fractional part of the emanation is removable by ebullition. An interesting case of this kind, which occurred in my laboratory, is referred to by Fletcher (*Phil. Mag.* June 1911, p. 770). A well-known similar case is recorded by Rutherford and Boltwood. It is probable that the deficient return of emanation observed when known amounts of radium are added to rock solutions, is due to other causes, for in this case there is no want of acidification. I here refer to the fact that a calibration constant obtained by boiling off the emanation from an acid solution of a rock to which a known quantity of radium has been added, is higher than if a like quantity of radium is treated in an acid, but otherwise pure aqueous solution. The quantities boiled off in the two cases may be about in the ratio of 6 to 8.

In addition to the foregoing objection the risk of contamination during the lengthy manipulation required in the preparation of the solutions is considerable. The very great labour involved in effecting the preliminary solution, and the final delay attending the regeneration of the emanation in the solutions are, perhaps, minor objections; but still they are serious in so far that where very many results are desirable the observer is often forced to be contented with an insufficient number.

For these reasons I have from time to time sought for some means of collecting from the rock the emanation originally prevailing in it, and with a minimum of manipulation and loss of time. Some years ago I found that the emanation could be collected from a rock while this was undergoing fusion and decomposition along with alkaline carbonates. Very encouraging results were obtained. In these experiments the powdered rock was mixed with 3 or 4 times its weight of the mixed carbonates of sodium and potassium, and enclosed in a platinum retort. The nozzle of the retort being kept cool by a water jacket, a rubber connexion could be attached to it, serving to convey the issuing gases to absorption-tubes containing soda-lime, and finally to a gas-

holder. Heating the retort for 40 or 50 minutes sufficed to fully complete the decomposition of the rock. There was difficulty experienced in obtaining a quite air-tight joint at the junction of the head and body of the retort.

Several experiments were subsequently made on the possibility of breaking up the powdered rock in the electric arc without the intervention of chemicals. But difficulties arose in securing complete volatilization. The action of the arc largely resulted in scattering the powder. For this and other reasons the method was abandoned as less reliable and controllable than the collection of the emanation during the decomposition of the rock in presence of chemicals. This latter method I determined to develop in connexion with the advantages arising from the use of the electric resistance furnace.

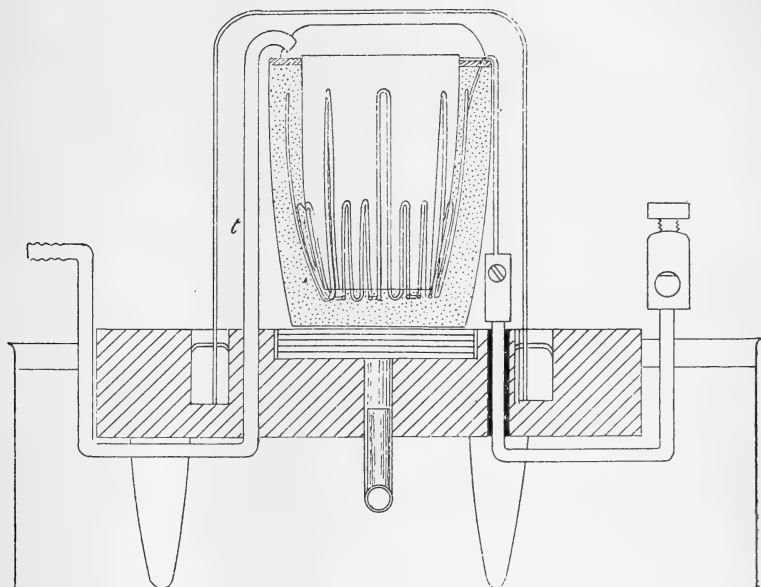
Two forms of this furnace have been tested. One of these is available for use with an ordinary platinum crucible; the other—of the tube-furnace pattern—requires the use of a special platinum boat. I shall first describe the former.

A disk-shaped base of iron has an annular groove turned in its upper surface. This groove receives a silica beaker or shade which is inverted over the crucible. Mercury poured into the groove renders the interior of the silica shade air-tight against small changes of pressure. The volume of air included beneath the shade amounts to about 500 or 600 c.c. The accompanying figure is to half-scale, so that the dimensions are readily obtained from it. The furnace is shown in vertical section. The disk is supported on short iron feet, and during an experiment stands in a vessel of water which maintains its temperature below that of the ebullition of water.

The platinum crucible is contained in an outer crucible of Berlin porcelain, a layer of magnesia powder intervening. In the magnesia powder the platinum resistance wire, which is heated by the current, is inserted. It is folded in a particular manner so as to supply the heat where most serviceable. A ring of asbestos card covers in the magnesia and supports a platinum cover or shield to reflect back heat and stop the spluttering of the melt injuring the clear silica shade. The outer porcelain crucible rests on several thicknesses of asbestos card contained in a recess on the surface of the iron disk. Beneath the supporting asbestos a perforation of the disk permits the escape of the evolved gases through a tube leading from the under side of the iron base. A groove is cut in the asbestos cards in such a manner as to leave a clear opening leading to the escape pipe; without this there is

risk of the moisture, which at first condenses in the asbestos, impeding the free escape of the gases.

Fig. 1.



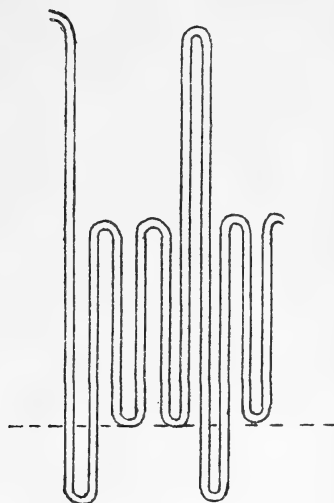
Connexion with the platinum resistance wire is made by two binding-screws placed beneath the silica shade, one of which is shown in the figure. This one is insulated from the iron base by a luting of fire-clay. The second binding-screw is screwed into the iron. A binding-screw screwed into the outer rim of the base makes connexion with it through the iron.

At the conclusion of an experiment it is desirable to wash out the interior of the shade by means of a stream of air directed into the crucible. The tube *t* enables this to be effected. It is closed without, until the conclusion of the experiment, when it is opened and air allowed to enter and flow through the furnace on its way to complete the filling of the electroscope.

The platinum resistance wire used in heating the crucible is about one metre in length and 1.2 mm. in diameter. It is folded in vertical folds, some folds being longer than others and some being partly bent in under the crucible. It is easy to give the right form to the wire. It is first

folded in zigzag according to a pattern as under (full size) laid down on a piece of paper. The folds beneath the dotted line are then bent at right angles to the paper, and the whole bent round the platinum crucible and pressed against its surface. This gives it the right set. This basket is placed in the porcelain crucible, resting on a layer of magnesia.

Fig. 2.



A little more magnesia is then added and the platinum crucible placed in position. Magnesia is next poured in around it and shaken down. The heater should be as close to the platinum as possible. This furnace is simple and effective, giving temperatures up to  $1200^{\circ}$ . The higher temperatures are, however, only got at the risk of shortening the life of the resistance wire. It would, doubtless, be better to imbed the wire in compressed magnesia, but this is not easy to effect without special appliances. The system of vertical folding is adopted chiefly for the reasons that it is easy thereby to distribute the heat as required, and that it is not attended by the gradual sagging downwards, which occurs when the wire is spirally folded and left unsupported by a rigid material.

It is desirable to watch the progress of the fusion lest there be risk of boiling over. For this purpose a small opening is made in the reflecting cover of platinum. The opening is to one side. The gases escaping from the furnace pass first into a small bulb to catch and hold back a certain amount of

water which is condensed over from the contents of the crucible. They then traverse two U-tubes filled with soda-lime, and finally, so far as not absorbed, enter a strong rubber bag. The thin rubber bags used for toy balloons will not do for this purpose as they soon develop dangerous leaks. The kind used for footballs is very suitable. The bag has to hold, without generating appreciable back pressure, about 600 c.c.

An experiment is carried out as follows:—The rock is ground so as to pass a sieve of 60 mesh to the inch and mixed with about four times its weight of the mixed carbonates of sodium and potassium. The mixture is introduced into the crucible and well shaken down. The crucible is then fitted into its mould in the magnesia powder, the cover placed in position, and finally the silica shade placed over all. The current may then be turned on and very gradually increased in intensity till a red heat is attained. At this stage time must be given for nearly complete evolution of the  $\text{CO}_2$  or there will be risk of boiling over. When the violent ebullition has subsided the temperature is still further increased till the interior of the crucible is at a bright yellow-orange or even pale yellow-white. The gases contained in the bag are then admitted into the exhausted electroscope, and when the bag is empty the tube *t* is opened and the pressure in the electroscope brought up to that of the atmosphere by air which has passed through the furnace and the absorption-tubes, washing out any residual emanation.

By inserting a platinum-palladium couple in the crucible I found that, in a typical experiment, the temperatures and durations of the same were as follows:—

Time from start.	Current (amps.).	Temperature.	
20 mins.	19	830°	Carbs. melting.
30 „	20	860°	Boiling.
50 „	21	900°	Boiling violently.
60 „	29	1150°	Yellow-white ; effervescence over.

The substance being dealt with in this experiment was a granite. It is evident that the greater part of the decomposition is effected at a temperature between 860° and 900°—a full red heat.

The effervescence in the case of a basic rock is not so intense nor so prolonged as when dealing with an acid rock. The addition of a couple of grammes of boracic acid (I owe

the suggestion to Prof. E. Werner) stirred into the charge in the form of powder, confers an intensity of effervescence upon it in no way inferior to that obtaining in the case of an acid rock.

In order to investigate the capabilities of this new method I took certain rocks which had recently been dealt with in my laboratory under circumstances in every way favourable to the solution method; no pains having been spared to obtain limpid solutions, and, finally, to effectively boil off the emanation. I refer to the rocks which entered into Mr. Fletcher's experiments on the granites of Leinster, and into his measurements of the radium in rocks of the Andes tunnel\*. The first serving as typical acid rocks, the latter as representing intermediate or basic rocks.

Before proceeding to these measurements it is evidently necessary to determine the calibration constant of the electro-scope by means of furnace experiments.

The electro-scope used for the purpose had previously been frequently calibrated by the solution method; uraninite of Joachimsthal having 64 per cent. of uranium being used. The calibrating solution in these tests was a highly dilute aqueous solution of the uraninite, containing some three or four milligrams of the ore and about 30 or 40 c.c. of redistilled HCl in 600 c.c. of distilled water. Such experiments gave for the constant of the electro-scope values generally varying closely about  $0.62 \times 10^{-12}$  gram. That is to say, a gain of one scale-division per hour corresponds to this amount of radium. It was also found that equally low constants were not obtained when the solution of uraninite was put into ordinary rock solutions or into sea water. The calibration constant then rose to  $0.8 \times 10^{-12}$ , or occasionally somewhat higher. This indicates the retention of some of the added emanation. The absolute values of these figures were found to be justified when the electro-scope was finally tested by a standard solution of radium which Professor Rutherford kindly sent me.

In finding the calibration constant of this electro-scope by a furnace experiment some of the same uraninite used in the preparation of the solution referred to above was mixed in the form of powder with an ordinary rock charge, and the experiment proceeded with in the usual manner. Subsequently a precisely similar charge, save that the uraninite was omitted, was dealt with in the furnace. The effect on

\* A. Fletcher, *Phil. Mag.* July 1910, and Jan. 1911.

the electroscope of the natural emanation derived from the last, expressed as so many scale-divisions gain per hour in the rate of discharge, is deducted from the like quantity observed in the first experiment. The difference gives the effect due to the uraninite, and enables the calibration constant of the electroscope to be arrived at.

In this manner the following values of the constant were obtained:—

0.70 mgrm.	uraninite in 10 grms.	granite (Glencullen)	$C=0.68 \times 10^{-12}$
0.72	"	" 7 " "	$C=0.55$ "
0.45	"	" 7 " "	$C=0.60$ "
Mean			$C=0.61$ "

The weighing of these small quantities of uraninite was effected on a delicate balance reading to 0.01 mgrm. under the conditions.

The variations seen in these experiments are sufficiently explained by the results of a microscopic examination of the powdered uraninite. It is then seen that the grains are very evidently heterogeneous in composition. Most of them are black and opaque or nearly so. These are doubtless the very pure oxide, and may contain quantities of uranium up to 85 per cent. Other particles are colourless and translucent or transparent. These are certainly impurities. Certain particles of pale yellow colour may represent altered uraninite. There are quite enough of these particles, both large and small, to render the chance considerable that in a very small quantity of the powder there might be a variation in the emanation content according to the percentage of impurities taken up. The average uranium content of this powder is 64 per cent. of uranium. While this result may safely be applied to such a considerable amount of it as would be taken for preparation of a standard solution, it might not rigidly apply to a fraction of a milligram of the powder.

By taking the mean of several such results the chemical analysis must, however, be applicable. It is probable that the mean of the three results is not far from the true constant. It appears to indicate for the fusion method a yield of emanation from an acid rock melt equal to that obtained from pure aqueous solutions. The temperatures reached in these experiments were about 1100° C.

Assuming this as the calibration constant, the following

are the results on certain granites treated as far as possible under exactly like conditions of heating.

	Wt. Grms. rock.	Wt. Grms. carbs.	By solution method.	By fusion method.
Granite, Ballyellin ...	10	25	$1.5 \times 10^{-12}$	$1.9 \times 10^{-12}$
„ „ ...	10	25	„	1.9 „
„ Glenmalure .	10	25	0.41 „	1.2 „
„ Killiney .....	10	25	1.76 „	1.8 „
„ Glencullen ...	10	25	1.2 „	2.3 „
		Means	1.22 „	1.8 „

The increase is 46 per cent. on the solution results.

A series of experiments on basic andesites were also made. It was evidently desirable to determine the calibration constant of the electroscope for substances differing so considerably from the granites in chemical composition. The following values were obtained:—

0.70 mgrm. uraninite, 10 grms. andesite, 25 grms. carbs.  $C = 0.79 \times 10^{-12}$ .

0.74 „ „ 10 „ andesitic tuff, 25 grms. carbs.

$C = 0.77 \times 10^{-12}$ .

0.67 mgrm. uraninite, 7 grms. Deccan trap, 28 grms. carbs.

$C = 0.75 \times 10^{-12}$ .

As these results stand appreciably higher than those obtained in the case of acid rocks I tried the effects of adding boracic acid:—

0.06 mgrm. uraninite, 6. grms. Deccan trap, 28 grms. carbs., 2 grms.

boracic acid,  $C = 0.60 \times 10^{-12}$ .

The effects of the boracic acid are remarkable; increasing the fluidity and effervescence and yielding a homogeneous melt. A further experiment was made with radioactive material prepared in a different manner. The melt from one of the experiments on the calibration constant with granites was weighed in its entirety, and 3 grams of it taken for admixture with 7 grams. of Deccan trap and



28 grams carbonates. As the entire melt weighed 28.28 grams and contained 0.72 mgm. uraninite, this represented  $16.62 \times 10^{-12}$  gram radium. From this, making the proper allowance for the weight of granite introduced along with the uraninite, the constant can be derived as before. Deducting for the leak due to the basic rock present, the constant was  $0.67 \times 10^{-12}$ . It appeared as if the added melt had the effect of increasing the fluidity or the ebullition.

The results on basic rocks by the fusion method show a great increase on those by solution:—

	Wt. of Rock, grms.	Wt. of Carbs., grms.	Result by Solution.	Result by Fusion.
Andesitic tuff ...	10	25	$1.11 \times 10^{-12}$	$3.8 \times 10^{-12}$
Same ...	5	20	„ „	3.8 „
Andesitic lava ...	10	25	0.36 „	2.0 „
		Means	0.74 „	2.9 „

It does not seem possible to question the very great increase obtained by the new method. The constant upon which the above results are based is  $0.77 \times 10^{-12}$ . This was used because the experiments were made without adding boracic acid. But even if the lowest value of the constant was used the increase on the solution method is remarkable. I would call attention to the exact agreement between the first and second results where a very considerable difference in the amount of rock and proportion of carbonates obtained.

An experiment on a Vesuvian lava from Colle Umberto, for which I had previously obtained  $14.6 \times 10^{-12}$  (Phil. Mag. Oct. 1909), gave with the new method  $25 \times 10^{-12}$ , or, if the lower constant is used,  $19.5 \times 10^{-12}$ .

Against the above consistently increased results has to be set some which I next carried out on the traps of the Deccan, using the same materials formerly dealt with. (British Assoc. Address Sec. C, 1908, and 'Radioactivity and Geology,' p. 42.) The result in this case was to lower the values originally found:—

	Result by Solution.	Result by Fusion.
Bedded basalt, Ghats .....	$2.7 \times 10^{-12}$	$2.2 \times 10^{-12}$
„ „ Pavagad Hill ...	8.2 „	3.2 „
Basalt dyke, Palasi .....	4.9 „	2.3 „
Bedded basalt, Palasdari.....	3.8 „	2.3 „
„ „ Keloli .....	2.4 „	1.5 „
„ „ Kasara.....	3.6 „	1.6 „
Means .....	4.3 „	2.2 „

I regard these last results as rather telling against the earlier values than against the method by fusion ; although I am unable to assign any cause for excess in the original determinations\*.

Some time after the completion of the foregoing experiments I obtained one of the tube-furnaces of the firm of Heræus. This furnace consists of a porcelain tube 5 cm. internal diameter and 30 cm. long, upon which is wound a ribbon of platinum, the whole being protected by a very effective lagging. It had originally been intended to carry out the fusions in an inner tube of porcelain or silica. It was found, however, that the first material allowed gas to diffuse in at high temperatures, and the second was attacked by the volatilized alkaline carbonates. Finally a platinum inner tube, prolonged by silver ends where the temperature was lower, had to be provided. The cost of this is a serious drawback to the use of these furnaces. The projecting ends being kept cool by a water-dropping arrangement and extending 10 centimetres beyond the heated part of the tube, may be closed with rubber stoppers. To protect these from radiated heat loose plugs of fireclay are inserted at each end before placing the stoppers in position. The rock charge is carried in a platinum boat half circular in section, with rounded ends ; it is 3 cm. in diameter, and 20 cm. in length. With proper precautions in raising the temperature 7 grams of rock and 28 grams of the carbonates may be dealt with in this boat, or even larger charges.

The end stoppers are fitted with tubes to lead off or admit gases. At one end the tube entering the stopper is a centimetre in diameter, and closed with a plate of glass so that a

\* Unless a rather improbable spurious leak due to the action of light on the sulphur insulation (an effect not known at the time) be responsible.

view may be obtained of the platinum boat during the progress of an experiment. To permit of this the fire-clay plug at this end is perforated centrally. A lateral and smaller tube, soldered to this wider tube, conveys the escaping gases to the soda-lime tubes and collecting-bag of rubber. The other stopper carries a tube which is kept closed till the conclusion of the experiment. Then when the transfer of the gas to the electroscope is completed and the rubber bag is quite empty, this tube is opened and the contents of the furnace washed out by a current of air into the electroscope.

In order to secure a better wash-out of the soda-lime tubes the connexions are so arranged that the contents of the rubber bag are first drawn back through the soda-lime tubes on their way to the electroscope, and when the bag is empty the wash-out air-current passing through the tube-furnace traverses the absorption-tubes in the other direction before admission to the electroscope. The diameter of the fusion-tube being 3.3 cm., its content of gas may be taken by an electroscope of between 600 and 700 c.c. capacity, and leave room in the electroscope for a sufficient wash-out of the furnace.

With the use of a metal inner tube the temperature reached in this furnace is hardly so high as that attained in the first described furnace. The current prescribed by the makers must not be exceeded. This gives in the inner tube a bright orange-yellow heat, which, as will presently be seen, seems nearly or quite as effective as the higher temperatures. The details of an experiment need not be described, they are essentially the same as in the case of the other furnace.

Working with this furnace Mr. Fletcher kindly made for me the following determinations upon samples of granite

Locality.	Wt. of Rock, grms.	Wt. of Carbs., grms.	Result by Solution.	Result by Fusion.
Killiney Hill .....	6	24	$1.76 \times 10^{-12}$	$2.9 \times 10^{-12}$
Glencullen .....	6	24	1.2    "	1.9    "
Glenmalure .....	6	24	0.41   "	1.0    "
Ballyellin .....	6	24	2.08   "	2.2    "
Aughrim .....	6	24	1.02   "	1.8    "
Blackstairs Mt.....	6	24	2.41   "	3.0    "
Same .....	6	24	"   "	3.0    "
		Means ...	1.48   "	2.13   "

which had been dealt with by the solution method in his experiments on the Leinster Granite (Phil. Mag. Jan. 1901).

The increase is 44 per cent. This, however, does not quite give the full increase. A low result by solution (1.14) on the Ballyellin granite was also obtained, and again the highest of 3 results is cited above in the case of the Glencullen granite solution. Allowance for this would raise the percentage increase by the new method. It is a striking fact that the Aughrim result is based on four repetition experiments on the one solution, giving precisely the same result, and yet the fusion method raises it by 66 per cent. The Blackstairs result is based on two identical determinations of the emanation in the solution. The agreement with my own results on some of these rocks by use of the other furnace is close.

In calculating the above results obtained by the tube-furnace, special experiments on the calibration constant proper to the furnace were made by Mr. Fletcher. Two are by addition of the uraninite before mentioned to the Blackstairs granite :—

0.34 mgrm. uraninite in 6 grm. granite,  $C = 0.62 \times 10^{-12}$

0.60    "    "    "    "    C = 0.57 × 10<sup>-12</sup>

On the strength of these results the constant would appear to be about  $0.6 \times 10^{-2}$ , and this value was taken for the foregoing determinations. The following calibration observations made on two standards which I had prepared some months previously are of interest:—

(1) A quantity of radium in solution =  $15.7 \times 10^{-12}$  gram. was added to 7 grms. of boracic acid. The mixture was dried over the water-bath and fused to a clear glass which was pulverized and preserved in a closed tube.

For the experiment this powder was added to 6 grams of the Glencullen granite mixed with the alkaline carbonates. The fusion gave  $C=0.73 \times 10^{-12}$ .

(2) One milligram of uraninite in solution, taken from the standard solution of the Joachimsthal ore, was added to 7 grms. of powdered Glencullen granite. This was then dried over the water-bath, mixed with carbonates, and fused. The melt was pulverized, weighed, and put by in a closed tube.

For the experiment 4 grams of this melt was added to 5 grams Killiney granite along with 24 grams carbonates.

Calculated directly, by deduction of the increased leak due to the granites present, the constant is found to be  $C=0.72 \times 10^{-12}$ ; which is in close agreement with the result

by (1). It is not improbable that the higher results in these two cases are due to a continuous and appreciable emanation loss from preparations of the kind.

Tests of the reagents used in the foregoing experiments were made. The carbonates were, indeed, from the same stock as had been used in the solution experiments on granites and andesites, and had been already several times tested by the solution method, yielding inappreciable or negligible traces of radium. Yet, owing to the more searching nature of the new method, I thought it advisable to again test the fusion mixture.

(1) Twenty-five grams of the mixed alkaline carbonates were fused and heated to the highest temperature of the furnace. There was no effect upon the electroscope; or, rather, there was a small negative effect, the normal leak falling slightly.

(2) Twenty grams of the mixed carbonates were mixed with 7 grams of precipitated silica and fused. In this experiment there was, of course, brisk effervescence. The electroscope observed for 21 minutes after admission of the gases showed no change in rate of discharge.

(3) An exact repetition of this experiment was made at a later date, when the effects were somewhat different. The rate of discharge before the experiment, which was not very steady, rose, after admission of the gases, 2 or 3 scale-divisions per hour. But there was no further change during three hours.

(4) In order to test the boracic acid used in some of the experiments, 7 grams of the powder were mixed with 28 grams of the carbonates and fused. The electroscope was in excellent condition, reading 4 scale-divisions per hour, with a slight tendency to an augmented rate just before admission of the gases. After transfer of the gases it rose to 6 per hour in 30 minutes, but then continually fell till in three hours it read 4.8 per hour. It is probable that this effect was not due to radium; in any case it is negligible. This test involves both the boracic acid and the carbonates.

The use of borax glass as a substitute for the carbonates having been kindly suggested to me by Professor the Hon. R. J. Strutt, an experiment was carried out in which 6 grams of the Blackstairs granite was fused with 24 grams of borax. The leak of the electroscope referable to the granite was in this experiment 34 per hour against 37 per hour with the carbonates. The use of the borax is, therefore, admissible, so far as the indications of this one experiment go. A slight deficiency of emanation yield, if there is any, would,

probably, be made good in the calibration constant as determined with the same reagent. Its use would possess the advantage that boiling over could not occur. On the other hand, the melt is not so readily removed from the boat or crucible ; solution appearing to be necessary.

The foregoing results appear to indicate that this method of collecting the emanation during decomposition and fusion is more searching than the method by solution. Its effectiveness is doubtless due to the small bulk of the materials dealt with, their very high temperature, and, in the case of the use of carbonates, to the intense effervescence attending decomposition. Acid rocks yield their emanation somewhat more freely than do basic rocks. This may be due to the fact that in the case of basic melts there is often a gravitational separation in the crucible ; a heavy layer, possessing very great viscosity even at the highest available temperatures, forming at the bottom. The use of boracic acid prevents this segregation, and gives a homogeneous melt as well as intense effervescence.

While there appears no doubt as to the more searching nature of the new method and little difficulty in accounting for its effectiveness, it is not easy to explain why the solution method gives a relatively deficient yield. One would fancy that the mode of determining the calibration constant would compensate for effects tending to conceal the emanation ; the added radium being exposed to the same causes of deficiency as affect the original radium in the rock. This may not be true, however. There might be a more or less constant amount of emanation held back in rock solutions, and this loss would then fall upon the yield when the rock content only was being investigated. The calibration experiment made with the chemically rich rock solution, in this case, would only reveal this phenomenon in so far as it might increase with the quantity of radium present. An actual concealment of some 30 per cent. on the yield of emanation from pure aqueous solutions is, in fact, observed.

There is another possibility. There may be more emanation in the alkaline solution than is boiled off. This would, *a priori*, seem a likely explanation ; but I have, so far, failed to find any support for it in experiments in which the alkaline solution was tested after acidification. But again, there may be causes leading to the failure of this test.

The fusion method seems not only more searching, it is less open to risk of contamination, for the preparation is limited to the pulverization of the rock. Its rapidity leaves nothing to be desired. If the crucible or boat is chilled after an

experiment, the melt is at once cleanly removable, and a fresh charge may be immediately placed in the furnace. Thus a succession of experiments may be carried out, the results being available in a little more than an hour after starting, if the maximum reading reached by the electroscope, about 15 or 20 minutes after admission of the emanation, is availed of.

The use of the fusion method in the convenient form described involves the assumption that there is no serious loss of emanation attending the pulverization of the material dealt with. Under the conditions this assumption seems fully justified. It is not necessary to grind the rock very fine. In the experiments cited above the rock powder was generally sifted through a sieve 60 mesh to the inch. Boltwood (Phil. Mag. April 1905) found that "very finely pulverized" radioactive minerals lost from 0.2 to 26 per cent. of emanation, and in a later paper (Am. Journ. Sc. xxx. April 1908) that the emanation loss in powdered uraninite varied from 1.4 to 14.1 per cent. Geiger and Rutherford (Phil. Mag. Oct. 1910) found that a sample of Joachimsthal pitchblende when finely powdered lost 6.2 per cent. of its emanation. These refer to substances brought to a very fine state of subdivision. The experiments which have been made upon the escape of helium from pulverized minerals are, very probably, quite applicable to escape of emanation. Now Moss determined that quantities up to one per cent. of the helium contained in a mineral could be liberated by grinding *in vacuo*. Strutt found that a quantity of monazite, powdered and passed through a wire-gauze sieve of 120 mesh to the inch, from immediately after grinding to 33 days later, showed a helium loss probably less than the 500th part of the whole. Lastly Gray (Proc. Roy. Soc. March 10, 1909) has made a careful quantitative examination of the helium loss attending different states of subdivision. Thus thorianite, of known helium capacity, reduced to very fine particles, ranging in size from 0.001 mm. to 0.030 mm., showed a loss of 5 per cent. of its helium. Gray concludes that when the size of the particles is greater than 0.01 mm. (1/250 inch) scarcely any helium is liberated. The liberation of the helium probably begins in the neighbourhood of 0.005 mm.

In order to test directly whether the anticipations founded upon the foregoing investigations were justified in the case of the rock powders, a quantity of the Deccan trap of Ghats, the radium content of which I had found to be  $2.2 \times 10^{-12}$  grm. per grm., was enclosed in a large U-tube. The powder had been put through the same sieve—60 mesh to the inch—used

in the furnace experiments. 96 grams of the powder were so enclosed. After more than a month the amount of emanation collected in the tube was investigated by exhausting an electroscope, after first carefully rating it, and filling it with air drawn slowly through the U-tube. The gain in the rate of discharge was less than 3 scale-divisions per hour; barely more than  $2\frac{1}{2}$ . This represents an amount of radium no more than  $1.5 \times 10^{-12}$  gram. The emanation in the 96 grms is about  $211 \times 10^{-12}$ . Hence the radium content of this powder, as determined by the emanation contained in it, would be underestimated by less than one per cent. The error is, of course, quite negligible.

The method of extracting radium emanation by fusion is applicable to other investigations than rocks and minerals. Natural waters, such as river waters, &c., would certainly be best dealt with by this method; the residues from large quantities, obtained by evaporation, being fused with carbonates in the furnace. For such delicate work small-sized furnaces are easily constructed. In the case of sea waters its use seems particularly desirable. Discrepancies arising from conditions of ebullition, acidification, presence of organic matter, or from whatever source, must assuredly disappear when the dry salts are treated in the furnace. In this case the bulk of the residue left by evaporation may be much reduced by evaporation of the chloride of sodium in an open crucible, and, I believe, without risk of loss of radium.

I hope to be able shortly to give results obtained by these applications of the fusion method.

I desire to thank Mr. W. Tatlow for much kind assistance in arranging for the supply of current required in the rather extensive series of preliminary experiments which I found it necessary to make: also Mr. L. B. Smyth for valuable help in carrying out the experiments.

X. *The Magnetic Field produced by a Charged Condenser moving through Space.* By W. F. G. SWANN, D.Sc., A.R.C.S., Assistant Lecturer in Physics at the University of Sheffield\*.

#### *Introduction.*

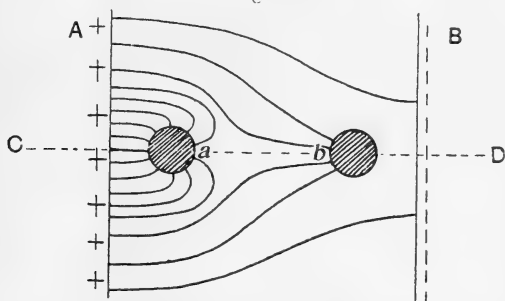
A SYSTEM of charged bodies moving through space with velocity  $v$ , should, on the assumption of a quiescent æther, give rise to a magnetic field which at each point is equal to  $4\pi vP$ , where  $P$  is the electric polarization at that

\* Communicated by the Author. Read at the Meeting of the British Association, 1910.



point resolved perpendicular to the velocity  $v$ . Röntgen endeavoured to detect this field by its effect on a magnetic compass-needle, but no such effect was observed. Sir Joseph Larmor has explained this by showing that the induced charge produced on the surface of the compass-needle is such as by its motion to completely annul the magnetic field produced by the charged bodies, at all points in the interior of the compass-needle. I think this can also be seen to follow from the consideration that, since all the bodies are moving in the same direction, and since all the tubes of force which strike the surface of the compass-needle end there, none of them exist within the compass-needle, to produce by their motion a magnetic field. Now although the magnetic field is incapable of being detected by a compass-needle, it seems at first sight that it might be capable of detection, by means of a rotating coil; for let AB (fig. 1) be two

Fig. 1.



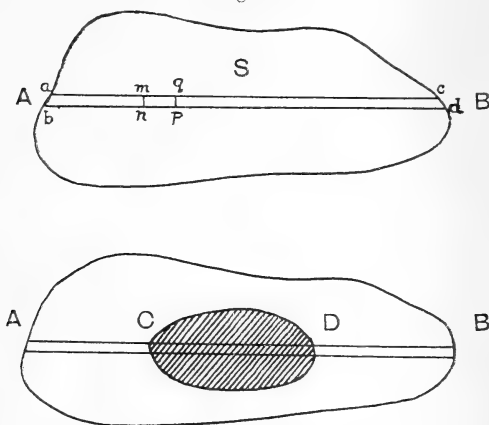
condenser-plates moving with the earth in a direction perpendicular to the plane of the paper, and imagine the coil shown in section to rotate about an axis CD. It is easy to see that the tubes of force will be distributed in the manner qualitatively illustrated in the figure, and it is not obvious that the magnetic flux produced by the motion of those tubes which strike the side  $b$  of the coil will be exactly cancelled by the flux caused by the motion of those tubes which bend round, and strike the coil on its inner side at  $a$ . Since the flux is certainly zero when the plane of the coil is perpendicular to the line of motion, we might expect on rotating the coil to obtain an alternating current which by suitable commutation could be detected by means of a galvanometer.

Unfortunately it appears on examination, that the flux through the coil is at all times zero, the two opposing portions annulling each other, as will be shown in Section I, provided that the whole of the space in the vicinity of the coil is filled with material of constant specific inductive

capacity. It will appear, however, (Section 2) that if part of the space inside the coil is filled with dielectric material of one kind, *e. g.* paraffin wax, and the other part with dielectric material of another kind, *e. g.* a vacuum, a resultant magnetic flux should be obtained through the coil, provided that the specific inductive capacity is a quantity which may be looked upon as continuous throughout the medium to which it refers. As will be shown later (Section 4), while the electron theory satisfies the requirements of a hypothetical dielectric of this kind, as far as the field outside it is concerned, nevertheless, inside the dielectric, the condition of continuity is not satisfied; and it will follow that on this view of dielectric action the flux through the coil in all positions will be zero, so that the absence of any effects of the kind sought in the experiments to be presently described affords direct proof of the discontinuous nature of the specific inductive capacity, and shows that dielectric action is to be accounted for by the presence of something of the nature of electric doublets, and cannot be attributed to any other mysterious power of twisting the tubes of force, which the dielectric might be imagined to possess.

Section 1. *The total magnetic flux through a closed circuit kept at constant potential, and due to the motion of a system of charged bodies along with the closed circuit, is zero, when the whole medium in the neighbourhood of the closed circuit is filled with a substance of constant specific inductive capacity K.*

Fig. 2.



Let S (fig. 2) be the circuit (not necessarily a plane circuit), and  $v$  its velocity in common with the system of

charged bodies. Draw two parallel planes across the circuit at a distance apart  $dy$ . Let these planes cut the circuit in the points  $acdb$ , and let  $mnpq$  be a rectangular element of  $acdb$ . Let  $\psi$  be the angle made at any point by  $v$  with the plane of  $mnpq$ , and let  $P$  be the electrical polarization resolved parallel to the long axis of  $acdb$ . On writing  $d\phi$  for  $\overline{mq}$  the magnetic flux through  $mnpq$  is

$$4\pi vP \cos \psi \cdot \overline{mn} \cdot dv.$$

Remembering that  $\overline{mn} \cos \psi = dy$  and writing  $F$  for the electric intensity corresponding to  $P$ , we have

$$\text{Magnetic flux through } mnpq = KF \frac{v}{c^2} dy \cdot dv.$$

Hence the total flux through  $acdb$

$$= \frac{Kv}{c^2} dy \int_A^B F dx,$$

$c$  being the velocity of light. Now  $F$ , which is the electric intensity corresponding to  $P$ , is composed of two parts, and may be written in the form  $X - v\gamma$ , where  $X$  is the part which is derivable from a potential, and which can produce mechanical force on a charge  $e$  moving with the system, while  $-v\gamma$  is a part whose mechanical force  $-v\gamma e$  on a charge  $e$  moving with the system is just counteracted by the mechanical force  $+v\gamma e$  exerted on the charge owing to its motion in the magnetic field,  $\gamma$  being the magnetic field resolved perpendicular to  $P$ . The field  $\gamma$  is of course also perpendicular to  $v$ . Since both ends of the strip  $AB$  are at the same

potential  $\int_A^B X dx = 0$ , so that

$$\begin{aligned} \text{Flux through strip} &= \frac{Kv}{c^2} dy \int_A^B (X - v\gamma) dx = \frac{Kv^2}{c^2} dy \int_A^B -\gamma dx \\ &= -\frac{Kv^2}{c^2} (\text{Flux through strip}). \end{aligned}$$

Hence the flux through the strip is zero, and since the whole curve  $S$  may be divided up into strips in this way, the total flux through it is zero\*.

\* The absence of any magnetic field in the interior of a conductor, *e. g.* the conducting compass-needle in Röntgen's experiment, due to the motion of charged bodies along with the conductor, is a particular case of this more general theorem.

Section 2. Case where  $K$  is variable.

Suppose now that a portion of the space within  $S$  (the shaded portion) is filled with material of specific inductive capacity  $K_2$ , the rest of the space being filled with material of S.I.C. equal to  $K_1$ . By an argument exactly similar to that given above, we arrive at the expression

$$\text{Total flux through strip} = \frac{v}{c^2} dy \int_A^B K(X - v\gamma) dx.$$

Thus, since  $K$  is not the same at all points along the strip, we have

Total flux through strip

$$\begin{aligned} &= K_1 \frac{v}{c^2} dy \int_A^C (X - v\gamma) dx + K_2 \frac{v}{c^2} dy \int_C^D (X - v\gamma) dx \\ &\quad + K_1 \frac{v}{c^2} dy \int_D^B (X - v\gamma) dx \\ &= K_1 \frac{v}{c^2} dy \int_A^B (X - v\gamma) dx + (K_2 - K_1) \frac{v}{c^2} dy \int_C^D (X - v\gamma) dx. \end{aligned}$$

Since  $\int_A^B X dx$  is zero, and since, as is very easily verified, the quantity  $v\gamma$  which itself arises from the motion of the system is only of the second order in  $\frac{v}{c}$  compared with  $X$ , the integrals of the form  $\int v\gamma dx$  are negligible, and we obtain

$$\begin{aligned} \text{Flux through strip} &= (K_2 - K_1) \frac{v}{c^2} dy \int_C^D X dx \\ &= (K_2 - K_1) \frac{v}{c^2} dy \left\{ \begin{array}{l} \text{Potential difference} \\ \text{between C and D} \end{array} \right\}. \end{aligned}$$

If we now draw an infinite series of lines perpendicular to the axis of  $y$ , each line connecting two parts of  $S$ , and if  $V$  represents the potential difference between the points where these lines enter and leave the intermediate dielectric, we have

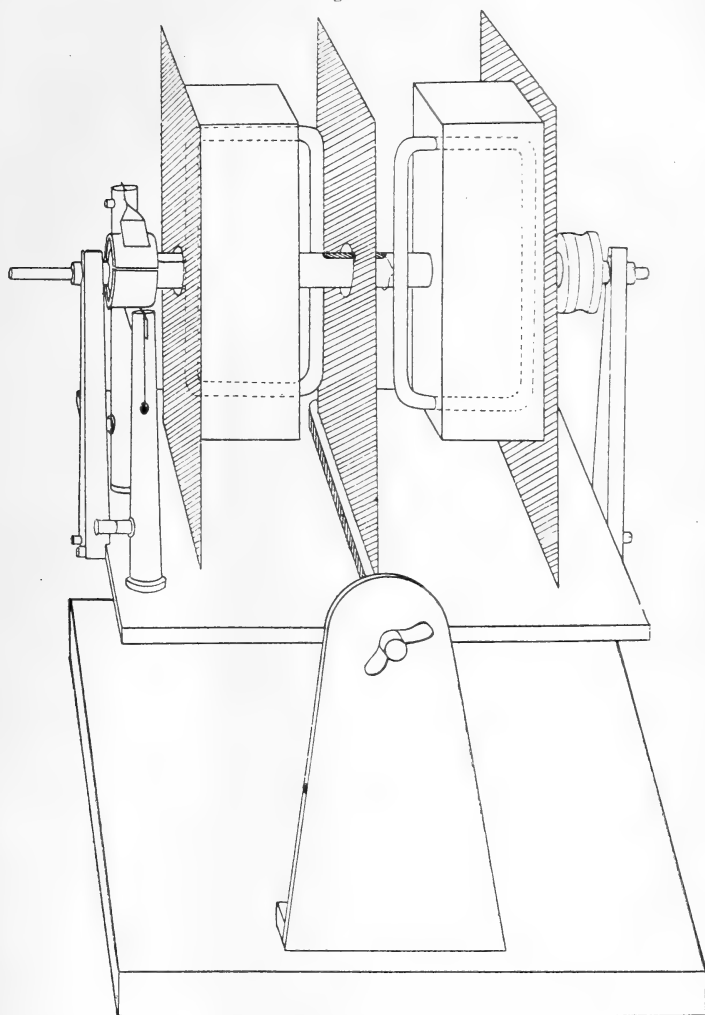
$$\text{Total Magnetic flux through } S = (K_2 - K_1) \frac{v}{c^2} \int V dy,$$

the integral being taken right across the circuit.

Section 3. *The Apparatus and the Experiment.*

After performing several experiments with a preliminary apparatus consisting of a single coil rotating between two condenser-plates, the form of apparatus shown in fig. 3 was

Fig. 3.



finally decided upon. Instead of one rotating coil there were two, each wound with about 300 turns of copper wire to a resistance of 36 ohms, the coils being afterwards bound

with silk, and shellacked. The coils were connected in such a way that on rotating them together the E.M.F.'s due to the earth's magnetic field acted in opposite directions round the circuit, so that the effect of this field was eliminated, and what is more important, any effects due to its fluctuations were automatically eliminated. The three vertical plates shown in the figure formed two condensers; the central plate, which was insulated in sulphur, could be charged, while the other two were fixed to a brass plate which could be earthed; thus any magnetic fluxes due to the earth's motion through space were additive in their effects on the galvanometer. The coils were partially embedded in rectangular blocks of paraffin wax, which also served to hold them in position, and they were arranged symmetrically with respect to the axis of rotation, so that the system was balanced when rotating. The galvanometer used was of the Broca type, and contained two coils each of resistance 32 ohms; these coils were arranged in series, and the point of junction was earthed. By earthing this point, and in virtue of the symmetry of the arrangement, various small leakage effects which caused trouble in the preliminary experiments were successfully overcome; for example, gradual leakage from the charged plate, and consequent alteration of the induced charge on the surfaces of the coils, resulted in electricity coming up from earth, and some of this came through the galvanometer, but in virtue of the symmetry of the above arrangement, equal quantities came through the two galvanometer coils, and consequently their effects on the galvanometer-needle cancelled.

The apparatus was mounted on a base as shown in the figure, in such a manner that it could be turned about, and the base could be clamped to the table in either a horizontal or a vertical plane by means of a nut. The rotating coils were connected by two pieces of copper foil cemented to the axle, which consisted of an ebonite rod with a brass core, and the system could be rotated by a motor placed 2 metres away.

The central plate, which was connected to the inner coating of a leyden-jar, was charged from a Wimshurst machine, one pole of which was earthed, and the potential of the plate was measured with a Kelvin electrostatic voltmeter.

It was necessary to carefully earth one pole of the wimshurst, as otherwise currents were produced through the tables &c., which were sufficient to cause slight kicks in the galvanometer when the condenser was charged or discharged. Kicks of this kind were not of vital importance, since they

did not affect the steady position of the zero, but nevertheless it was convenient to reduce them to a minimum.

Gradual leakage of electricity from the charged plate could not result in any permanent alteration in zero, even when the coil was rotating, for, in view of the fact that the charging connexion was made to the central plate at the top, the magnetic flux through the coil due to such leakage would be parallel to the brass base of the apparatus, and even if its magnitude were worth considering, it could produce no effect on the rotating coil. Only magnetic flux perpendicular to the brass base could produce any effect on the rotating coil, since the commutator was fixed so that when the planes of the coils were parallel to the brass plate, a line joining the commutator slits was perpendicular to it.

*Method of making the experiment.*

It was first necessary to set the apparatus so that a line parallel to the brass base, and perpendicular to the axis of rotation, should be parallel to the direction of the æther drift.

Professor Trouton, in connexion with his work on the "Couple exerted on a Charged Condenser moving through Space"\*, has determined the time of the day throughout the year at which the æther drift is parallel to the earth's surface, and he also gives the azimuth of the drift, and its magnitude, taking into account the Sun's orbital and proper motions. Though his calculations refer to London, it is sufficient for the purpose in hand to take them as applying to Sheffield. It is easy to find from Trouton's data the time at which the drift is vertical, and the experiments in this paper were always performed when the drift was either horizontal or vertical.

The apparatus having been adjusted to the correct position, and the commutator having been well wetted with paraffin oil, the motor was started. Any deflexion produced by want of complete compensation of the coils was balanced by magnets placed slightly asymmetrically, about 1.5 metres away. The central plate was then charged, say positively, to about 4000 volts, as recorded by the electrostatic voltmeter. The zero of the galvanometer having been read, the plates were discharged by two knobs placed some distance away, and any alteration in the galvanometer reading was noted. The experiment was repeated several times, and another series was then taken with the central plate charged negatively. The whole apparatus was then turned through 180 degrees, so that any magnetic field due to the earth's motion was

\* Phil. Trans. A. 1904, p. 165.

reversed through each coil, and the experiments were repeated. A measurement of the time of swing of the galvanometer completed the set of observations.

*Magnitude of the effect to be expected due to the  
Earth's Motion.*

The expression for the maximum flux through the coil, given on page 154, becomes

$$\frac{1}{9} \times 10^{-12} v (k-1) \int V dy,$$

where  $k$  and 1 are the specific inductive capacities of paraffin wax and air respectively, and  $V$  is in volts.

If  $l$  is the length of the line formed by the intersection of the plane of the coil with the dielectric, and if  $\bar{V}_1$  and  $\bar{V}_2$  are the respective mean values of the potentials over the corresponding lines for the two coils, we have

Maximum flux through the two coils

$$= B = \frac{1}{9} \times 10^{-12} v l (k-1) (\bar{V}_1 + \bar{V}_2).$$

The method of measuring  $\bar{V}_1$  and  $\bar{V}_2$  is explained on page 162.

In order to determine the magnitude of the deflexion which the above flux should produce when the coils rotate, it was best to short-circuit one of the coils (which was done by means of a brass collar connecting the copper strips joining the coils), set the other coil in rotation in such a position as to be affected only by the earth's vertical component, and observe the deflexion  $\delta_2$  produced on the galvanometer. A high resistance was put in series with the galvanometer, and the pair were shunted for this purpose.

Let  $R_2$  be the resistance of the circuit containing the single unshort-circuited coil and the shunted system,  $G$ ,  $Z$ , and  $S$  the resistances of the galvanometer, the coil in series with it, and the shunt respectively; let  $a$  be the effective mean area of the coil,  $n_2$  the frequency of rotation of the coil, and  $W$  the vertical component of the earth's field; then the required deflexion which would be produced by the flux  $B$  is easily seen to be

$$\delta_1 = \left[ \frac{\delta_2 n_1 R_2 (G + Z + S)}{n_2 R_1 W a S} \right] \left[ \frac{1}{9} \times 10^{-12} v l (k-1) (\bar{V}_1 + \bar{V}_2) \right] \frac{T_1^2}{T_2^2},$$

where  $R_1$  is the resistance of the two rotating coils and the galvanometer in series,  $n_1$  is the frequency of rotation in the main experiment,  $T_1$  and  $T_2$  are the times of swing of



the galvanometer in the main and subsidiary experiment respectively.

In view of some uncertainty as to the effective resistance of the commutator when rotating\*, the precaution was taken of placing in series with the rotating coil in the subsidiary experiment, such a resistance as to make the resistance of the circuit containing the shunted galvanometer and the rotating coil the same as the resistance of the circuit composed of the galvanometer and the two rotating coils in the main experiment. Thus the quantities  $R_1$  and  $R_2$ , which contain the resistance of the commutator, cancelled out.

The value of  $\delta_2$  was obtained by reversing the current through the galvanometer, and taking half the deflexion observed.

The accompanying table shows the values of  $\frac{\delta_2}{n_2}$  obtained in three successive experiments; the constancy of the numbers in the last column gives an idea of the degree of consistency of the readings.

Speed revs., per min.	Deflexion on reversal.	$\frac{\delta_2}{n_2}$
735	230	0.156
800	253	0.158
800	248	0.155

$$\text{Mean } \frac{\delta_2}{n_2} = 0.156$$

The time of swing of the galvanometer was 11.0 seconds, and the value of  $\frac{R_2(G+Z+S)}{R_1S}$  was 280, so that in view of the fact that  $W=0.44$ ,  $k=2.3$ ,  $a=31.3$ ,  $l=8$  cms., we find for the deflexion to be expected in the main experiment, for a case where  $v=18$  miles per second ( $2.9 \times 10^6$  cm./sec) †,  $\bar{V}_1 + \bar{V}_2 = 1200$  volts,  $n_1=800$ , and  $T_1=11$  seconds,

$$\delta_1 = 10.2.$$

\* The commutator was kept well wetted with paraffin oil while running, to keep its effective resistance constant.

† The fact that the resultant velocity of the æther drift happened to coincide with the velocity (18 miles per second) of the earth's orbital motion, is a mere coincidence; the directions were of course not the same.

*The Results†.*

The following tables show the results obtained in the main experiments. The third column represents the deflexion observed on discharging the central plate of the apparatus, and the fourth column the values calculated in the above manner. 0 is written when the deflexion is less than 0·5 division. Such very slight deflexions as were observed are doubtless due mainly to alterations of zero due to incomplete astaticism of the galvanometer-needle, to lack of compensation of the two coils as far as fluctuations of the earth's field are concerned, and to residual electrostatic effects. There is obviously no evidence of any appreciable deflexion; the very slight irregular deflexions observed are hardly to be wondered at, in view of the facts that the galvanometer had a time of swing of 11 seconds, the scale was 3 metres away, and the central plate was charged to 4000 volts.

Continued repetition of the experiments seemed unnecessary, as the observations below were taken after much experience with the apparatus. The main part of the work

TABLE I.

Experiments performed on July 20, 2.40 A.M. to 3.40 A.M.  
Æther drift vertical.  $T_1 = 11\cdot4$  seconds.

Central plate charged positively.				Central plate charged negatively.			
Speed revs. per min.	Potential of central plate. Volts.	Deflexion observed.	Deflexion calculated.	Speed revs. per min.	Potential of central plate. Volts.	Deflexion observed.	Deflexion calculated.
810	+4000	0	10·4	810	-4000	+2	10·4
810	...	0	10·4	740	...	+2·5	9·5
800	...	-2	10·3	740	...	+2	9·5
800	...	-3	10·3	750	...	0	9·6
800	...	0	10·3	760	...	0	9·8
800	...	-1·5	10·3	740	...	+1	9·5
800	...	+0·5	10·3	720	...	+0·5	9·2
800	...	-4*	10·3	710	...	+2	9·1
800	...	0	10·3				
800	...	0	10·3				

\* The spot of light was unsteady when this observation was taken.

† The calculated values of  $\delta_1$  given in the tables are obtained on the assumption that  $k=2\cdot3$ . The value of  $k$  as measured, without taking any precautions to prevent soaking, was higher than this. If the larger value were used the calculated values of  $\delta_1$  would be greater; it was considered safer, however, in view of the possibility of soakage, to take the value of  $k$  usually given in the tables for the kind of wax used.

TABLE II.—Apparatus turned through  $180^\circ$ .

Central plate charged positively.				Central plate charged negatively.			
Speed revs. per min.	Pot. of central plate. Volts.	Deflexion observed.	Deflexion calculated.	Speed revs. per min.	Pot. of central plate. Volts.	Deflexion observed.	Deflexion calculated.
720	+4000	+1	9.2	720	-4000	0	9.2
730	...	0	9.3	720	...	-3	9.2
720	...	+1	9.2	720	...	0	9.2
700	...	-3	9.0	710	...	0	9.1
680	...	+1.5	8.5	710	...	+2	9.1
680	...	+1.5	8.7	700	...	-1	9.0
690	...	0	8.9	710	...	0	9.1
680	...	0	8.7	700	...	0	9.0

TABLE III.—Experiments performed on July 20, 2.55 P.M. to 4.20 P.M.  
Æther drift horizontal.  $T_1 = 10.6$  seconds.

Central plate charged positively.				Central plate charged negatively.			
Speed revs. per min.	Pot. of central plate. Volts.	Deflexion observed.	Deflexion calculated.	Speed revs. per min.	Pot. of central plate. Volts.	Deflexion observed.	Deflexion calculated.
690	+4000	+2	7.7	750	-4000	+3	8.4
740	...	-3	8.2	760	...	-1.5	8.5
700	...	+1	7.8	760	...	-1	8.5
700	...	0	7.8	780	...	0	8.7
690	...	-1	7.7	760	...	0	8.5
680	...	+0.5	7.6	700	...	+2.5	7.8
780	...	+1	8.7				
740	...	-1	8.2				

TABLE IV.—Apparatus turned through  $180^\circ$ .

Central plate charged positively.				Central plate charged negatively.			
Speed revs. per min.	Pot. of central plate. Volts.	Deflexion observed.	Deflexion calculated.	Speed revs. per min.	Pot. of central plate. Volts.	Deflexion observed.	Deflexion calculated.
770	+4000	0	8.6	860	-4000	+1	9.6
740	...	+1	8.2	880	...	-1	9.8
730	...	0	8.1	880	...	+2	9.8
810	...	+4	9.0	870	...	+4	9.7
810	...	0	9.0	850	...	0	9.5
830	...	+2	9.2	860	...	+3	9.6
810	...	-2.5	9.0	840	...	+2	9.4
820	...	+2	9.1	800	...	0	8.9
840	...	-2	9.4				

consisted in overcoming the various causes of fluctuation due to direct electrostatic effects, variations of the earth's field, &c., and once these had been successfully overcome, it was felt that multiplication of the observations could not add anything to the reliability of the results.

*Method of measuring the quantity  $\bar{V}$  referred to on page 158.*

The method adopted was to measure the potential at various points along the line joining the inner point of intersection of the coils with the paraffin wax, then by plotting the potential against the distance from one end of this line, the quantity  $\bar{V}$  representing the mean value of the potential could be obtained.

In order to measure the potential at any point along the above line a special method was adopted, since the introduction of anything of the nature of a wire connected to an electrometer of any appreciable capacity would result in such an induced charge on the wire as would completely alter the potential to be measured.

A small proof plane (about 3 mms. in diameter) was placed at the point at which the potential was required, and was then touched by a thin earth-connected wire. The proof plane received an induced charge, and its potential became zero. Now assuming that the induced charge did not appreciably alter the distribution of electricity on the charged plate, and on the coil in its vicinity, which assumption was quite justified to the degree of accuracy to which we were working, we could look upon the potential of the proof plane, which was zero, as being made up of two equal and opposite parts: (1) the positive potential which would have existed at the point at which we desired the potential, if the plane had been absent, (2) the negative potential which the charge on the proof plane contributed. If the earth-connected wire were then removed the potential of the proof plane would still be approximately zero, except in so far as the small amount of charge on the wire itself contributed to the potential of the plane\*. If the proof plane were now removed and held away from the apparatus, it would have a potential as much below zero as the potential which we desired to measure was above zero. It only remained to measure the potential of the proof plane.

For this purpose an electrometer of small capacity was constructed. It consisted of a silvered glass fibre, with a

\* The error due to this cause became automatically eliminated in practice (see note on page 163).

silvered glass ball, 0.5 mm. in diameter, at each end, which was suspended by an insulating suspension, and provided with a mirror, for obtaining the deflexions. Another silvered glass ball was fastened to a piece of thin platinum wire, which was insulated by sulphur. When this fixed ball was charged it attracted one of the movable balls, and the sensitiveness of the arrangement could be adjusted by moving the fixed ball by a tangent screw.

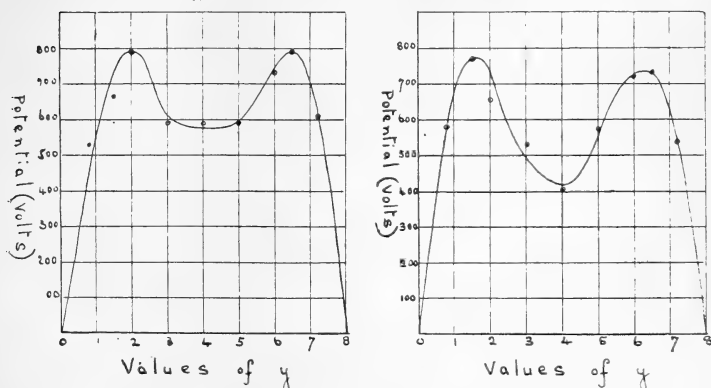
The proof plane whose potential was required was caused to touch the wire connected to the fixed ball, and the deflexion  $\alpha$  was observed. The electrometer was standardized by taking a series of readings in which the fixed ball was touched with the proof plane after the latter had been raised to known potentials by allowing it to touch a thin wire connected to the central condenser plate of the apparatus. The potential of this plate, which was of course reduced to potentials varying from 400 to 1000 volts, was measured by the electrostatic voltmeter\*.

Tables V. and VI. give for the two blocks the deflexions referred to as  $\alpha$  above, corresponding to the potential  $E$  of the central charged plate given in the first column. The third column gives the potentials corresponding to these deflexions, and the last columns the distances  $y$  of the points at which the potentials were measured, from one of the points of intersection of the coil with the paraffin wax.

The curves (fig. 4) represent the observations plotted

Fig. 4.

Curves showing the variation of potential with the distance  $y$ .



\* It will be seen that the error due to neglect of the part of the potential of the proof plane contributed by the charge on the wire, just cancels the error referred to in the note on page 162.

graphically, the dips in the middle being due to the brass axle which passed through the centre of the rotating system. From these curves we find for a difference of 4000 volts between the central and external condenser plates, the values  $\bar{V}_1 = 588$  volts  $\bar{V}_2 = 543$  volts. A slight error in the determination of the positions of the maxima of the curves is not of great importance in view of the sharpness of the maxima. The slight difference in the values of  $\bar{V}$  for the two coils is not surprising in view of the large shielding effect of the earthed coils, and consequent rapid variation of the potential in the vicinity of, and in a direction perpendicular to, the surfaces of the dielectrics along which the potentials were measured.

TABLE V.

E.	$\alpha$ .	V Volts.	$y$ .
4000	22	530	0.8
...	37	665	1.5
...	56	790	2.0
...	28	590	3.0
...	28	590	4.0
...	28	590	5.0
...	47	733	6.0
...	56	790	6.5
...	30.5	610	7.2

TABLE VI.

E.	$\alpha$ .	V Volts.	$y$ .
4000	27	580	0.8
...	53	770	1.5
...	36	655	2.0
...	22	530	3.0
...	13	405	4.0
...	26	575	5.0
...	45	720	6.0
...	47	733	6.5
...	23	540	7.2

#### Section 4. *The Nature of Dielectric Action.*

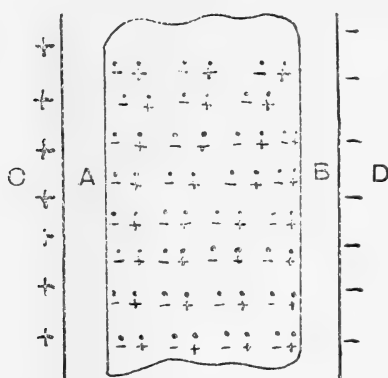
It may at once be remarked that the theorem proved in section 1 shows that if the whole of dielectric action is to be attributed to electric charges in the dielectric, the motion of the system through space cannot produce a magnetic flux through a closed circuit kept at constant potential. It is, I think, nevertheless interesting to verify the conclusion by a rather closer examination of the phenomenon of dielectric action, with a view to a clearer physical coordination of the various quantities involved.

We will first define specific inductive capacity in the following way. Let there be two large parallel condenser plates C, D either moving through space or at rest; let one plate be charged and the other earthed. Let  $V_1$  be the potential difference between two planes A and B situated between and parallel to the two plates. Now fill the space between A and B with a slab of material, and let  $V_2$  be the new potential difference between A and B. Then the specific inductive capacity of the material is  $K = \frac{V_1}{V_2}$ .

Now there are two distinct classes of action which will explain the existence of the quantity  $K$ . We may consider that the electric force causes a separation of positive and negative electricity in each atom or molecule, giving rise to something equivalent to a doublet, or we may imagine the doublets to exist even in the absence of the electric force, in which case they will be orientated at any instant in all sorts of directions, the effect of the electric force being to give them a preference towards an orientation of their axes in one particular direction. We shall first proceed to develop the consequences of the former hypothesis.

Considering the two condenser plates referred to above, with the slab of dielectric between them, we are to look upon the electric force as causing an electrical separation, giving rise to a series of doublets, arranged in the manner shown (fig. 5). Now the tubes of force from  $C$  do not pass continuously through the dielectric, most of them, or possibly all,

Fig. 5.



end on some or other of the negative charges on the doublets on the surface of  $A$ , and just as many tubes emanating from the positive elements of these doublets are so to speak freed, thus being at liberty to carry on the flux in the direction from  $A$  to  $B$ . If we were to cut a cylindrical hole in the dielectric with its axis perpendicular to  $A$ , and of length small compared with its cross-section, and if we were to measure the electric intensity in this hole, we should get  $4\pi c^2$  times the ordinarily defined polarization or number of tubes of force per square centimetre\*, we should get the

\* The polarization is here in electromagnetic units.

quantity whose line integral across the dielectric is  $K$  times the potential difference between  $A$  and  $B$ .

Viewing the matter from the standpoint we have adopted, we are driven to the conclusion, that though the dielectric acts at all points outside it or at a point in a hole inside it as though the tubes did actually pass continually through it, nevertheless, they do not run continuously in this way; in fact, between the elements of a doublet the tubes actually pass in the opposite direction to the ordinarily defined polarization. At each point inside the material of the dielectric, we must look upon the number of tubes of force per square centimetre as being algebraically made up of two parts: (1) the number ordinarily defined as the polarization, and (2) the number contributed in the opposite direction by the separation of the two kinds of electricity in the doublets. At any point outside the dielectric the second set is of course absent. The first set is equal to  $\frac{KF'}{4\pi c^2}$ , where  $F'$  is the electric intensity as ordinarily understood, at a point within the dielectric. The second set  $N'$  is such that

$$\int_R^S \frac{K}{4\pi c^2} F ds - \int_R^S N ds = \frac{1}{4\pi c^2} \left( \begin{array}{c} \text{Potential difference} \\ \text{between R and S} \end{array} \right) = \frac{1}{4\pi c^2} \int_R^S F ds,$$

so that

$$\frac{K-1}{4\pi c^2} \int_R^S F ds = \int_R^S N ds,$$

where  $F$  and  $N$  are the resolved portions of  $F'$  and  $N'$  along the path  $RS$ , along which the integral is taken, for it is to be remembered that we are admitting no mysterious method of modifying the force in the dielectric other than that due to the charges. The physical effect of the doublets is to reduce the work which we should do in taking a unit of electricity from  $R$  to  $S$ , since when between the elements of a doublet we should be assisted in our journey, the effect being greater, the greater the moments of the doublets; and to the extent that we may assume the effect produced by the doublets to be proportional to the potential difference  $V$  which would exist between the planes of opposite faces of the dielectric if the dielectric were absent and the charges on  $C$  and  $D$  were the same as at present, we may write  $\Delta V$  (the lowering of the potential difference between the faces) as  $\Delta V = pV$ , where  $p$  is a constant. The specific inductive capacity will then be  $\frac{V}{V-\Delta V}$  or  $\frac{1}{1-p}$ .



Returning to the argument on page 154 we are now to realize that in taking the flux through the strip we are to take account of the true polarization at each point in the dielectric, and our expression for the flux through the strip AB becomes

$$\text{Flux} = 4\pi v dy \int_A^B P dx,$$

where  $P$  is the resolved portion of the true polarization in the direction  $dx$ . Now, as we have seen,  $P$  is made up of two parts  $\frac{KF}{4\pi c^2}$  and  $-N$ , so that

$$\begin{aligned} \text{Flux through strip} = \frac{v}{c^2} dy \left[ \int_A^C (K_1 F - 4\pi c^2 N) dx + \int_C^D (K_2 F - 4\pi c^2 N) dx \right. \\ \left. + \int_D^B (K_1 F - 4\pi c^2 N) dx \right] \end{aligned}$$

and since as we have seen

$$\frac{(K-1)}{4\pi c^2} \int F dx = \int N dx$$

over any path, the above equation becomes

$$\text{Flux through strip} = \frac{v dy}{c^2} \int_A^B F dx = \frac{v dy}{c^2} \int_A^B f dx = \frac{v dy}{c^2} \int_A^B (X - v\gamma) dx,$$

where  $X$  and  $\gamma$  have the significance accorded them on page 153, and  $f$  is the true electric intensity corresponding to  $F^*$  at a point in the dielectric.

Since 
$$\int_A^B X dx = 0,$$

we have

$$\text{Flux through strip} = -\frac{v^2}{c^2} dy \int \gamma dx = -\frac{v^2}{c^2} dy (\text{Flux}),$$

from which it follows that the flux through the strip is zero.

\*  $f$  is the  $x$  component of the actual force at a point; it is a quantity varying rapidly from point to point, being in fact in opposite directions on the two sides of an element of a doublet.  $F$  is the ordinarily defined, smoothed out value of this electric force. It can only be realized as  $\frac{\delta V}{\delta s}$  where  $\delta V$  is the alteration of potential in the length  $\delta s$ ,  $\delta s$  being a length small compared with ordinary dimensions, but large compared with the distance between two doublets. The line integrals of  $f$  and  $F$  over any finite path are of course the same.

We thus see that the part of the flux represented by

$$-4\pi v dy \int_A^B N dx$$

is just such as to annul the other portion represented by

$$\frac{v}{c^2} dy \left[ \int_A^C K_1 F dx + \int_C^D K_2 F dx + \int_D^B K_1 F dx \right],$$

the equivalent of which we found for the total flux on page 154. If we prefer a rather less exact but more vivid picture of the phenomenon, we may say that the total magnetic flux produced by the motion of the tubes of force between the elements of individual doublets, is just equal and opposite to the magnetic flux produced by the motion of the tubes joining different doublets. Considering the second view in which the doublets exist, but are orientated at a haphazard manner in the absence of the electric force, we must look upon them as being turned on the application of the electric force so that their axes tend to point on the average in one direction, to an extent depending on the electric force. It is easy to see that the effect of this orientation of the doublets is to reduce the potential difference which would exist between the opposite faces of the dielectric for the same distribution of charge on the charged plates, and to the extent that this reduction  $\Delta V$  is proportional to  $V$ , we may write

$$\frac{V}{V - \Delta V} = \frac{V}{V - pV} = \frac{1}{1 - p} = \text{constant} = K.$$

The argument showing the absence of any magnetic flux through a strip joining two points at the same potential follows in a manner exactly similar to that given above. On any conceivable view, in which dielectric action is to be explained entirely by the presence of electric charges in the dielectric, the expression  $\int_A^B P ds$  must equal  $\frac{1}{4\pi c^2} \int_A^B f ds$ ,

where the integral is taken along any path between A and B, and the quantities  $P$  and  $f$  represent the components of the polarization and of the true electric intensity at a point within the dielectric respectively, and as we have seen this latter integral vanishes when A and B are at the same potential, so that on no theory of this kind can we obtain any resultant magnetic flux through the closed circuit referred to on page 154, due to the motion through space of a system of charged bodies along with the circuit.

XI. *The Initial Accelerated Motion of a Rigidly Charged Dielectric Sphere.* By G. H. LIVENES, B.A., *Lecturer in Mathematics, Sheffield University* \*.

IN a previous paper† the problem of the motion of a perfectly conducting sphere was solved, and it was seen that the analysis and results were capable of expression in a manner quite independent of any "material" mass that the sphere might possess. The same method is now applied to the initial accelerated motion of a dielectric sphere with a rigid uniform charge of electricity. The notation of the previous paper is adopted, and in addition we use  $K$  for the specific inductive capacity of the medium of which the sphere is composed.

We proceed in an exactly analogous manner and assume for the field external to the sphere

$$X = \frac{e}{r^2} + \frac{2 \cos \theta}{r^3} (rf' + f),$$

$$Y = \frac{\sin \theta}{r^3} (r^2 f'' + rf' + f),$$

$$c\gamma = \frac{\sin \theta}{r^3} (r^2 f'' + rf'),$$

where  $f$  is in general a function of  $(ct - r + a)$ . Inside the sphere we have a field which is, in general, composed of both converging and diverging waves.

We assume

$$X = \frac{2 \cos \theta}{r^3} [r(\phi_1' - \phi_2') + \phi_1 + \phi_2],$$

$$Y = \frac{\sin \theta}{r^3} [r^2(\phi_1'' + \phi_2'') + r(\phi_1' - \phi_2') + \phi_1 + \phi_2],$$

$$c'\gamma = \frac{\sin \theta}{r^3} [r^2(\phi_1'' + \phi_2'') + r(\phi_1' - \phi_2')],$$

where  $\phi_1$  is a function of  $(c't - r)$  and  $\phi_2$  a function of  $(c't + r)$ , and  $K = c^2/c'^2$  defines  $c'$  as the velocity of radiation in the dielectric.

\* Communicated by the Author.

† Phil. Mag. May 1911, p. 640.

The conditions to be satisfied are :

1. That the field in the sphere has to remain regular at the origin  $r=0$ . This requires

$$\phi_1(c't) + \phi_2(c't) = 0.$$

2. That the field is continuous at the boundary of the outgoing wave, which requires, just as before,

$$f(0)=0, \quad f'(0)=0.$$

3. The conditions at the surface of the sphere. These are two in number :

(i.) The tangential electrodynamic force is continuous. In the case under discussion, in which the sphere starts from initial rest with a small acceleration, this condition is the same as that the tangential electric force is continuous to the first order. This gives in the usual way

$$a^2 f'' + a f' + f - e \xi = a^2 (\phi_1'' + \phi_2'') + a (\phi_1' - \phi_2') + \phi_1 + \phi_2$$

at  $r=a$ .

(ii.) The discontinuity in the normal induction is  $\frac{e}{4\pi a^2}$ ; this gives

$$a f' + f - e \xi = K [a (\phi_1' - \phi_2') + \phi_1 + \phi_2]$$

at  $r=a$ .

The particular integral of these last two equations subject to

$$\phi_1(c't) + \phi_2(c't) = 0$$

is

$$f(ct) = \frac{es}{2c^2} \left[ c^2 t^2 - 2act + \frac{4a^2}{K+2} \right],$$

$$\phi_1(c't-a) = -\frac{es}{4ac^2} \cdot \frac{1}{K+2} [(c't-a)^3 + 3a^2(c't-a) + 5a^3],$$

$$\phi_2(c't+a) = \frac{es}{4ac^2} \cdot \frac{1}{K+2} [(c't+a)^3 + 3a^2(c't+a) + 5a^3].$$

There is then the complementary integral of the equations determined with  $\xi=0$ . To obtain these we try solutions

$$\begin{aligned} f &= B e^{\lambda \left( \frac{c't-r+a}{a} \right)}, \\ \phi_1 &= B' e^{\lambda' \left( \frac{c't-r}{a} \right)}, \\ \phi_2 &= -B' e^{\lambda' \left( \frac{c't+r}{a} \right)}, \end{aligned}$$

which satisfy the condition

$$\phi_1(c't) + \phi_2(c't) = 0.$$

They satisfy the conditions at the boundary of the sphere if

$$\lambda c = \lambda' c',$$

and also

$$B(1 + \lambda + \lambda^2) = B'[(1 + \lambda' + \lambda'^2)e^{-\lambda'} - (1 - \lambda' + \lambda'^2)e^{\lambda'}],$$

$$B(1 + \lambda) = KB'[(1 + \lambda')e^{-\lambda'} - (1 - \lambda')e^{\lambda'}],$$

and thus  $\lambda$  and  $\lambda'$  must also satisfy

$$K \frac{1 + \lambda + \lambda^2}{1 + \lambda} = \frac{(1 + \lambda' + \lambda'^2)e^{-\lambda'} - (1 - \lambda' + \lambda'^2)e^{\lambda'}}{(1 + \lambda')e^{-\lambda'} - (1 - \lambda')e^{\lambda'}},$$

which leads to the period equation

$$\tanh(K^{\frac{1}{2}}\lambda) = K^{\frac{1}{2}}\lambda \left[ 1 + \frac{K\lambda^2(1 + \lambda)}{(K - 1)(1 + \lambda) - K\lambda^3} \right],$$

which is the equation obtained by Walker in the particular case of no charge or no motion. The equation was originally derived and discussed by Lamb (*Camb. Phil. Trans.* 1899). It may be shown to have a root zero, but no others except complex ones whose real part is negative. Thus the vibratory terms ultimately disappear and the solution is expressed solely in terms of the particular integral.

The general solution for the field is thus obtained, to the order specified, by a combination of the particular integral previously obtained with the complementary integral consisting essentially of the real part of a sum

$$\sum B_r e^{\lambda_r \left( \frac{ct - r + a}{a} \right)}$$

taken over the infinite number of roots of the above equation in  $\lambda$ .

To obtain the force on the sphere we have to proceed rather more carefully than before. Walker fully discusses the point in terms of the Maxwell stress system, but it seems that it can be at once deduced in the same form as for the conducting sphere, viz.,

$$P = \frac{2}{3} \frac{e}{a} f'' \quad \text{at } r = a,$$

by considerations of the force acting across a sphere just enclosing the given dielectric sphere. Now

$$f = \frac{es}{2c^2} \left[ x^2 - 2ax - \frac{4a^2}{K + 2} \right] + \sum B_r e^{\lambda_r \frac{x}{a}},$$

where  $x = ct - r + a$ , and  $\sum$  is taken over all the roots of the

period equation in  $\lambda$ , the real part of the sum being alone retained. Thus

$$P = \frac{2}{3} \frac{e}{a} \left[ \frac{es}{c^2} + \sum \frac{\lambda_r}{a^2} B_r e^{\lambda_r \frac{ct}{a}} \right].$$

As we have seen above the exponential terms representing vibrations soon die away, and we are left with the equation of motion in the form

$$P = \frac{2}{3} \frac{e^2}{ac^2} s,$$

from which we deduce that the electromagnetic mass of the sphere is

$$\frac{P}{s} = m = \frac{2}{3} \frac{e^2}{ac^2},$$

which agrees with the value previously obtained for the quite different perfectly conducting sphere.

A few general remarks on the solution here obtained seem necessary.

It will be noticed that the general form of the  $f$  function involves an infinite number of arbitrary constants  $B_r$ , corresponding to the infinite number of roots of the period equation. Moreover, we have only two conditions to determine these constants. In addition to those already written down we have the two conditions for the continuity at the outgoing wave boundary. These give

$$\sum B_r + \frac{4a^2}{K+2} \frac{es}{2c^2} = 0,$$

$$\sum \lambda_r B_r - 2a^2 \frac{es}{2c^2} = 0.$$

The problem thus appears to contain a great degree of indeterminateness. It is, however, to be noticed that the conditions of the problem are also really very indefinite. The system really comprises an infinite number of degrees of freedom, corresponding to the bodily motions of the sphere and the infinite number of possible oscillatory motions which may exist in it. The geometrical conditions only involve the motion of the sphere as a whole and leave wholly unspecified the conditions under which the oscillations are taking place. If the method of distribution of the energy and momentum among these possible degrees of freedom could be specified, then the problem would be determinate. A study of the problem discussed by Lamb, where similar

oscillations occur on a sphere with no charge, throws some light on the point here involved.

The subject is, however, rather irrelevant to the main objects of this paper and need not be pursued. As before stated, the oscillations which do occur are very soon damped out, and we have then only to deal with the quite determinate particular solution of the equations involved.

The problem of the sphere accelerated from any initial velocity can easily be deduced from that given above if attention is paid to the few remarks offered by Walker in explanation of the single difficulty involved.

In a third and concluding paper I intend to give solutions on the above lines of the various types of oscillatory motion discussed by Walker. A short account of the radiation taking place from the various motions under review will also be added.

Sheffield,  
March 14th, 1911.

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XII. *Proposed Method for the better practical Application of Fourier's Theorem concerning the Roots of an Algebraical Equation.* By L. R. MANLOVE \*.

HOW to determine the situation and number of the real roots of any equation is a problem which has engaged the attention of many mathematicians.

"Sturm's Theorem" is a complete solution of the problem, but its application to equations of a high degree is very laborious.

"Fourier's Theorem" (it has been said) "has the advantage that the auxiliary functions employed in it can be formed by inspection, so that the method can be applied nearly with equal ease to an equation of any degree. The objection to this method is that by its immediate application we only find a limit which the number of real roots in a given interval cannot exceed, and not the actual number; and that the subsidiary propositions by which this defect is supplied are not of the same simple character as the original theorem."

It is suggested that the following method provides a simple practical substitute for the "subsidiary propositions" above referred to, thus completing Fourier's Theorem and, perhaps, making it fit to replace Sturm's Theorem in the textbooks.

\* Communicated by the Author.

The process may be shortly described as follows:—

(a) Ascertain by Fourier's original theorem the pairs of consecutive integers between which the roots must lie.

(b) Where the number of roots in any interval is doubtful proceed as if approximating by Lagrange's method to the roots in that interval. The real roots will be separated; the imaginary roots will lead to derivative equations which can be seen to have unity for the superior limit of their positive roots.

(c) Apply the test for equal roots only if and when in the course of the investigation the existence of equal roots appears probable.

It is submitted that the process is as systematic as that of Sturm's theorem without involving the labour frequently required by Sturm's method.

Equations of the 17th and 18th degrees have been treated without difficulty by Fourier's theorem with the modification described above.

#### EXAMPLE.

$$x^6 - 6x^5 + x^4 + 50x^3 - 62x^2 - 104x + 170 = 0.$$

(Positive roots.)

$$f(x) = x^6 - 6x^5 + x^4 + 50x^3 - 62x^2 - 104x + 170,$$

$$f'(x) = 6x^5 - 30x^4 + 4x^3 + 150x^2 - 124x - 104,$$

$$f''(x) = 30x^4 - 120x^3 + 12x^2 + 300x - 124,$$

$$f'''(x) = 120x^3 - 360x^2 + 24x + 300,$$

$$f^{IV}(x) = 360x^2 - 720x + 24,$$

$$f^V(x) = 720x - 720,$$

$$f^{VI}(x) = 720.$$

$x.$	$f.$	$f'.$	$f''.$	$f'''.$	$f^{IV}.$	$f^V.$	$f^{VI}.$
3	+	+	+	+	+	+	+
2	+	-	+	-	+	+	+
1	+	-	+	+	-	0	+
0	+	-	-	+	+	-	+



There are four changes of sign lost between 2 and 3 :

Put  $x = 2 + \frac{1}{u_1}$ .

1	-	6	+	1	+	50	-	62	-	104	+	170
2	-	8	-	14	+	72	+	20	-	168		
-	4	-	7	+	36	+	10	-	84	+	2	
+	2	-	4	-	22	+	28	+	76			
-	2	-	11	+	14	+	38	-	8			
+	2	+	0	-	22	-	16					
0	-	11	-	8	+	22						
+	2	+	4	-	14							
+	2	-	7	-	22							
+	2	+	8									
+	4	+	1									
+	2											
+	6											

The equation in  $u_1$  is (say)

$$F_A(u_1) = 2u_1^6 - 8u_1^5 + 22u_1^4 - 22u_1^3 + u_1^2 + 6u_1 + 1 = 0,$$

$$F_A'(u_1) = 12u_1^5 - 40u_1^4 + 88u_1^3 - 66u_1^2 + 2u_1 + 6,$$

$$F_A''(u_1) = 60u_1^4 - 160u_1^3 + 264u_1^2 - 132u_1 + 2,$$

$$F_A'''(u_1) = 240u_1^3 - 480u_1^2 + 528u_1 - 132,$$

$$F_A^{IV}(u_1) = 720u_1^2 - 960u_1 + 528,$$

$$F_A^V(u_1) = 1440u_1 - 960,$$

$$F_A^{VI}(u_1) = 1440.$$

$u_1$ .	F.	F'.	F''.	F'''.	F <sup>IV</sup> .	F <sup>V</sup> .	F <sup>VI</sup> .
1	+	+	+	+	+	+	+

*See Smoker*  
 $F_A(u_1)$  has no positive roots greater than unity; hence there are no real roots of  $f(x)=0$  between 2 and 3, and, as there is no other interval in which positive roots can exist, we may pronounce that there are no positive roots of  $f(x)=0$ .

EXAMPLE (continued).

(Negative roots.)

Put  $x = -y$  in  $f(x)$  and its derived functions and we have

$$\phi(y) = y^6 + 6y^5 + y^4 - 50y^3 - 62y^2 + 104y + 170 = 0,$$

$$\phi'(y) = 6y^5 + 30y^4 + 4y^3 - 150y^2 - 124y + 104,$$

$$\phi''(y) = 30y^4 + 120y^3 + 12y^2 - 300y - 124,$$

$$\phi'''(y) = 120y^3 + 360y^2 + 24y - 300,$$

$$\phi^{IV}(y) = 360y^2 + 720y + 24,$$

$$\phi^V(y) = 720y + 720,$$

$$\phi^{VI}(y) = 720$$

$y.$	$\phi.$	$\phi'.$	$\phi''.$	$\phi'''.$	$\phi^{IV}.$	$\phi^V.$	$\phi^{VI}.$
3	+	+	+	+	+	+	+
2	+	-	+	+	+	+	+
1	+	-		+	+	+	+
0	+	+	-	-	+	+	+

Two changes of sign are lost between 2 and 3.

$$\text{Let } y = 2 + \frac{1}{v_1}.$$

1 + 6 + 1 - 50 - 62 + 104 + 170
2 + 16 + 34 - 32 - 188 - 168
+ 8 + 17 - 16 - 94 - 84 + 2
2 + 20 + 74 + 116 + 44
+ 10 + 37 + 58 + 22 - 40
2 + 24 + 122 + 360
12 + 61 + 180 + 382
2 + 28 + 178
14 + 89 + 358
2 + 32
16 + 121
2
18

The equation in  $v_1$  is—

$$2v_1^6 - 40v_1^5 + 382v_1^4 + 358v_1^3 + 121v_1^2 + 18v_1 + 1 = 0,$$

which may also be written

$$2v_1^4(v_1^2 - 20v_1 + 191) + 358v_1^3 + 121v_1^2 + 18v_1 + 1 = 0;$$

and as the expression in brackets is positive for all real values of  $v_1$  we may pronounce that there are no positive roots of the equation in  $v_1$ ; therefore no real roots of  $\phi(y) = 0$  between 2 and 3; hence no negative roots of the original equation. All the roots of that equation are therefore imaginary.

### XIII. *Lines of Force due to given Static Charges.*

By Prof. D. N. MALLIK, B.A., Sc.D., F.R.S.E.\*

[Plate II.]

1. **D**IAGRAMS of lines of force due to given static charges are given at the end of the first volume of Maxwell's Treatise, in which also a brief description is given of a method of drawing them [Art. 123, vol. i.]. The importance of the subject, however, justifies a more detailed treatment, and I have, accordingly, in the present paper considered with considerable fulness, a simple geometrical method of drawing these lines which is obviously suggested by the construction given in Roget's 'Electricity' for Magnetic Curves.

2. Consider two charges  $e_1, e_2$  at A, B (Pl. II. fig. I.).

If  $F_1, F_2$  are the forces due to  $e_1, e_2$  at any point P, of which the coordinates are  $r_1, \theta_1, r_2, \theta_2$  respectively referred to A, B, we have, since the resultant force along the normal to a line of force vanishes,

$$F_1 r_1 \frac{d\theta_1}{ds} + F_2 r_2 \frac{d\theta_2}{ds} = 0, \quad . \quad . \quad . \quad (1)$$

$$\text{i. e.} \quad \frac{e_1}{r_1} \cdot \frac{d\theta_1}{ds} + \frac{e_2}{r_2} \cdot \frac{d\theta_2}{ds} = 0.$$

But

$$\frac{r_1}{r_2} = \frac{\sin \theta_2}{\sin \theta_1},$$

from the triangle APB.

\* Communicated by the Author.

We have, accordingly,

$$e_1 \sin \theta_1 d\theta_1 + e_2 \sin \theta_2 d\theta_2 = 0$$

$$\text{or} \quad e_1 \cos \theta_1 + e_2 \cos \theta_2 = \text{constant.} \quad . \quad . \quad . \quad . \quad (2)$$

If  $\theta, \theta'$ , are the interior angles of the triangle APB, we get

$$e_1 \cos \theta - e_2 \cos \theta' = \text{constant.}$$

This form of the equation enables us to give a simple geometrical construction for these lines.

### 3. CASE I.—Two equal and opposite charges.

Here,  $e_2 = -e_1$ .

The equation is  $\cos \theta + \cos \theta' = \text{const.}$

Divide AB into any number of equal parts  $\mu$ , say, and let  $AB = \mu a$ .

Produce AB to C, and BA to D, so that  $AC = BD = qa$ , where  $q$  is as much larger than  $\mu$ , as possible.

With A, B as centres and radii equal to AC, BD describe two circles.

Divide BC, AD into parts, each equal to  $a$ , and draw perpendiculars so as to meet these circles.

Number the points of intersection of these lines with either circle, viz. 1, 2, 3 &c., beginning with the lowest, on the side remote from the centre of the corresponding circle, and join these points to the same centre.

Calling now these numbers, the *index* numbers of these lines, we have the following rule:—

The points of intersection of the two sets of lines, such that the sum of their index numbers is constant, lie on a line of force.

For let  $r$  and  $s$  be the index numbers of any two lines from A and B respectively, intersecting at P.

And let  $\theta, \theta'$  define the point P (measured from the initial line in opposite directions—one counter-clockwise, (say) the other clockwise).

Then, confining ourselves to the points on one side of the axis,

$$qa \cos \theta = (q-r)a,$$

$$qa \cos \theta' = (q-s)a.$$

$$\therefore \quad \cos \theta + \cos \theta' = 2 - \frac{r+s}{q} = \text{const.}, \text{ if } r+s \text{ is constant.}$$

In the figure I.,  $p = 2$ ,  $q = 6$ .

(a) Putting  $\theta' = 0$ , we have

$$\cos \theta = 1 - \frac{r+s}{q},$$

and  $\theta$  is obviously the inclination of the tangent to a line of force at A.

Now,  $\theta$  is imaginary if  $r+s > 2q$ .

(b) If  $\theta' = \pi$ ,

$$\cos \theta = 3 - \frac{r+s}{q};$$

and in this case  $\theta$  is imaginary if  $\frac{r+s}{q} < 2$ ,

$$\text{or } > 4.$$

Hence we conclude that lines of force for which  $r+s > 2q$  are those situated on one side of AB and those for which  $r+s$  lies between  $2q$  and  $4q$  are situated on the other side of AB.

#### 4. CASE II.—Two unequal opposite charges.

Here,  $e_2 = -e'$ ,  $e_1 = e$ .

The equation is

$$e \cos \theta + e' \cos \theta' = \text{const.}$$

We have only now to take  $AC = qa$  and  $BD = q'a$  (fig. II.), such that

$$\frac{q}{q'} = \frac{e}{e'}.$$

For obviously if  $\theta, \theta'$  define any point P, satisfying the condition  $r+s = \text{constant}$ , as in case I., we have, as before,

$$qa \cos \theta = (q-r)a,$$

$$q'a \cos \theta' = (q'-s)a.$$

$$\therefore q \cos \theta + q' \cos \theta' = (q+q'-\overline{r+s}),$$

$$\text{or } e \cos \theta + e' \cos \theta' = \text{const.}$$

5. Suppose  $q > q'$ .

Putting  $\theta = 0$

$$\text{we have } q' \cos \theta' = q' - \overline{r+s}.$$

$$\text{Or, } \cos \theta' = 1 - \frac{r+s}{q'};$$

( $\theta'$  being the inclination to the axis of the tangent to a line of force at B).

Now,  $\theta'$  is imaginary, if  $r+s > 2q'$ .

That is, the lines of force issuing from  $e$  at A will not converge to  $e'$  at B, when  $r+s > 2q'$ .

If

$$r+s = 2q',$$

we have

$$q \cos \theta + q' \cos \theta' = q - q'.$$

Transferring to bipolars,  $\rho$  and  $\rho'$ , we have

since

$$a^2 + \rho'^2 - 2a\rho' \cos \theta = \rho^2$$

and

$$a^2 + \rho^2 - 2a\rho \cos \theta' = \rho'^2,$$

$$\frac{a^2 + \rho'^2 - \rho^2}{2a\rho'} q + \frac{a^2 + \rho^2 - \rho'^2}{2a\rho} q' = q - q',$$

$$\text{or } (a + \rho - \rho') \left[ (a + \rho + \rho') \frac{q'}{\rho} + (a - \rho' - \rho) \frac{q}{\rho'} \right] = 0;$$

*i. e.*, the line of force corresponding to  $r+s=2q'$ , consists of

$$(1) \quad a + \rho - \rho' = 0,$$

which is the portion of the axis beyond A and B, and

(2) the curve

$$(a + \rho + \rho') \frac{q'}{\rho} + (a - \rho' - \rho) \frac{q}{\rho'} = 0.$$

This curve intersects the axis,  $a + \rho - \rho' = 0$ , at the point defined by

$$\frac{q'}{\rho^2} = \frac{q}{\rho'^2},$$

*i. e.*, it passes through the point of equilibrium.

The line  $r+s=8$  in the fig. II. (where  $q=12$ ,  $q'=4$ ) obviously separates the lines which converge to  $e'$  (at B) and those which do not so converge.

( $\theta$  is imaginary if  $r+s > 2q$ , but the maximum number of lines is only  $2q$ , therefore all the lines issue from A.)

#### 6. CASE III.—(Two equal charges of the same sign.)

Here,

$$e_1 = e_2 = e.$$

The equation is

$$\cos \theta - \cos \theta' = \text{constant}.$$

The same construction being made, as in the first case, the index numbers corresponding to the centre B have to be marked 1, 2, 3, &c. beginning on the same side as B, that is, both counter-clockwise.

For, if  $\theta, \theta'$ , as before (3) define P,

$$qa \cos \theta = (q-r)a$$

$$-qa \cos \theta' = (q-s)a.$$

$$\therefore \cos \theta - \cos \theta' = 2 - \frac{r+s}{q}.$$

Putting  $\theta' = 0$ , we have  $\cos \theta = 3 - \frac{r+s}{q}$ .

Or,  $\theta$  is imaginary, if  $r+s < 2q$  or  $> 4q$ , i. e.  $r+s$ , equal to or greater than  $2q$  define the lines which alone issue from one of the charges and the rest from the other.

For  $r+s = 2q$ , we have  $\cos \theta - \cos \theta' = 0$ .

This is the line of force, passing through the point of equilibrium, bisecting the line joining the two charges.

7. CASE IV.—Let the charges be unequal and of the same sign.

The construction is the same as in case II.; only the index numbers corresponding to the centre B have to be marked as in case III., i. e. both counter-clockwise.

We have  $qa \cos \theta = (q-r)a$ .

$$-q'a \cos \theta' = (q'-s)a.$$

$$\therefore q \cos \theta - q' \cos \theta' = (q + q' - r + s),$$

$$\text{i. e., } e \cos \theta - e' \cos \theta' = \text{constant.}$$

Put  $\theta' = 0$ .

$$\text{Then } \cos \theta = 1 + \frac{2q' - r + s}{q},$$

and  $\theta$  is imaginary if  $2q' > r + s$ .

That is,  $r + s =$  or  $< 2q'$ , define the lines which do not issue from A.

$$\text{If } r + s = 2q', \quad q \cos \theta - q' \cos \theta' = q - q'.$$

As in case II., the bipolar equation of the line is

$$(a - \rho' - \rho) \left[ (a - \rho' + \rho) \frac{q}{\rho'} - (a - \rho + \rho') \frac{q'}{\rho} \right] = 0,$$

$$\text{i. e., } a - \rho' - \rho = 0,$$

or the portion of the axis between A and B and

$$(a - \rho' + \rho) \frac{q}{\rho'} - \frac{a - \rho + \rho'}{\rho} q' = 0.$$

The latter can be shown to pass through the point of equilibrium on the axis and to separate the two sets of lines which issue from the points A and B. In the fig. III.,

$$q = 15, \quad q' = 5,$$

$$\text{and} \quad r + s = 10$$

separates the two sets of lines.

#### 8. CASE V.—A charge $e$ in a uniform field.

From the equation

$$e \cos \theta - e' \cos \theta' = \text{constant},$$

we have

$$e \cos \theta + \frac{e'}{r^2} r^2 (1 - \cos \theta') = \text{constant},$$

where  $r$  is the distance of any point P on a line of force from  $e'$ .

This gives,

$$e \cos \theta + \frac{e'}{r^2} \left[ \frac{r^2 \theta^2}{2} + \dots \right] = \text{constant}.$$

Now, when  $r$  is infinite,  $r\theta = y$ ,

$y$  being the ordinate of the point P, with AB as the axis of  $x$ , drawn parallel to the direction of the lines of force due to the uniform field and  $\frac{e'}{r^2} = -X$ , where  $X$  is the uniform force acting in the field, measured along AB.

The equation thus becomes

$$e \cos \theta - \frac{Xy^2}{2} = \text{constant}.$$

9. This can also be obtained directly from the differential equation: thus, if  $R, \theta$  are the polar coordinates of any point P, we have

$$\frac{e}{R^2} \cdot R \frac{d\theta}{ds} + X \frac{dy}{ds} = 0,$$

$$\text{i. e.,} \quad \frac{e}{R} d\theta + X dy = 0.$$

But since  $y = R \sin \theta$ , we have

$$e \sin \theta d\theta + Xy dy = 0,$$

$$\text{i. e.,} \quad e \cos \theta - \frac{Xy^2}{2} = \text{constant}.$$



10. Put

$$\frac{2e}{X} = qa p,$$

the equation then becomes

$$qa \cos \theta - \frac{y^2}{p} = \text{constant}.$$

This leads to the following construction :—

Draw the lines from A, having the charge  $e$ , with index numbers 1, 2, 3, &c. as before.

Along the axis of  $y$ , lay off lengths  $\sqrt{pa}$ ,  $\sqrt{2pa}$ ,  $\sqrt{3pa}$ , .... and through their extremities draw parallels to the axis of  $x$ , and let these have index numbers 1, 2, &c. Then the points of intersections of these two sets of lines, such that the sum of their index numbers is constant, lie along a line of force.

For, if P is a point defined by index numbers  $r$  and  $s$ , we have

$$qa \cos \theta = (q-r)a,$$

$$y = \sqrt{pas}.$$

$$\therefore qa \cos \theta - \frac{y^2}{p} = \{q - r + s\}a = \text{constant},$$

since  $r + s$  is constant.

11. A practical method of laying off lengths  $\sqrt{pa}$ ,  $\sqrt{2pa}$ , &c., along the axis of  $y$ , will obviously be to describe the parabola  $y^2 = px$  (say on the negative side of the axis of  $x$ ) and measure off lengths  $-a$ ,  $-2a$ , along this axis. Then, the corresponding ordinates will be of lengths  $\sqrt{pa}$ ,  $\sqrt{2pa}$ , &c.

12. Putting  $y = 0$ , we have

$$\cos \theta = 1 - \frac{r+s}{q},$$

where  $\theta$ , as before, is the inclination of the tangent to a line of force at A, to the axis of  $x$ ; and  $\theta$  is imaginary, if  $r + s > 2q$ :

i. e., lines of force corresponding to  $r + s > 2q$  do not issue from  $e$ .

If  $r + s = 2q$ , the equation of the corresponding line of force becomes

$$qa \cos \theta - \frac{y^2}{p} = -qa;$$

and changing into Cartesians

$$\left(\frac{y^2}{p} - qa\right)^2 = \frac{a^2}{p} \left(2aq - \frac{y^2}{p}\right).$$

This is, obviously, a curve, passing through

$$x^2 = \frac{1}{2} qap, \quad y = 0.$$

But since

$$\frac{2e}{X} = qap,$$

this is obviously the point of equilibrium.

This curve also divides the lines of force into two sets, those issuing from  $e$ , and those that do not issue from  $e$ .

In the fig. IV.,  $q = 14, p = 8a$ .

The line of force through the point of equilibrium is defined by  $r + s = 28$ .

13. We may also obtain the equation (2) in a slightly different manner.

Let  $d\omega_1$  be the solid angle of an elementary tube issuing from  $e_1$ .

$$\text{Then} \quad F_1 dS = e_1 d\omega_1,$$

where  $dS$  is the normal section of the tube at P.

$$\text{But} \quad dS = r_1 d\theta_1 dz,$$

if  $dz$  is an element of length, perpendicular to the plane APB, and  $r_1, \theta_1$  are polar coordinates of P referred to  $e_1$ .

Hence

$$F_1 r_1 d\theta_1 dz = e_1 d\omega_1.$$

$\therefore$  equation (1) of art. 2 reduces to

$$e_1 d\omega_1 + e_2 d\omega_2 = 0;$$

$$\text{i. e.,} \quad e_1 \omega_1 + e_2 \omega_2 = \text{constant.}$$

Let  $N_1$  = whole number of tubes issuing from  $e_1$ ; then  $N_1 = e_1$ ; and if  $n_1$  = number of tubes corresponding to  $\omega_1$ ,

$$\frac{\omega_1}{4\pi} = \frac{n_1}{N_1};$$

$$\text{i. e.,} \quad e_1 \omega_1 = 4 \cdot \pi \cdot n_1.$$

$\therefore$  the equation can be written

$$n_1 + n_2 = \text{constant.}$$

14. Comparing this with the equation  $r + s = \text{constant}$ , defining a line of force, we notice that the index numbers enumerate the lines of force issuing from a charged point, on an assumed scale, ranging from the initial line joining the charges, in either direction, according to the signs of the charges.

Maxwell's method of drawing the lines of force is based on this principle. [See also Mascart and Joubert's treatise, vol. i. ch. vii.]

15. It is, now, obviously possible to generalize the equation. Thus with three charges,  $e_1, e_2, e_3$ , the lines of force are given by

$$e_1 \omega_1 + e_2 \omega_2 + e_3 \omega_3 = \text{constant},$$

or 
$$n_1 + n_2 + n_3 = \text{constant}.$$

In order to trace the curves, we have first to draw the lines corresponding to the charges  $e_1, e_2$  (say), and then draw the tubes corresponding to  $e_3$  (*i. e.*, lines with index numbers, as before) intersecting the lines of force due to the first two.

The points of intersection of these two sets of lines, such that the sum of the index numbers of the three charges is constant, will be on a line of force.

16. We may write the above equation in the form

$$q_1 \cos \theta_1 + q_2 \cos \theta_2 + q_3 \cos \theta_3 = (q_1 + q_2 + q_3 - \overline{r + s + t}),$$

where  $r + s + t = \text{constant}$  defines a line of force.

Moreover,  $\theta_1, \theta_2, \theta_3$  are all measured from the initial line, clockwise or counter-clockwise, according as the charges are *negative* or *positive*.

17. We shall consider the particular case in which  $e_2$  is negative and is situated between  $e_1, e_3$  which are to be both positive.

In this case,  $\theta_2$  is measured clockwise and  $\theta_1$  and  $\theta_3$  are measured counter-clockwise. In other words, the index numbers corresponding to  $q_2$  on the one hand and those for  $q_1, q_3$  on the other, are enumerated as in case II.

18. Putting  $\theta_1 = 0, \quad \theta_3 = \pi,$

we have 
$$q_2 \cos \theta_2 = q_2 + 2q_3 - \overline{r + s + t}$$

or 
$$\cos \theta_2 = 1 + \frac{2q_3 - \overline{r + s + t}}{q_2},$$

where  $\theta_2$  is the inclination to the axis of the tangent to a line of force at  $e_2$ .

Now  $\theta_2$  is imaginary,

(1) if 
$$2q_3 - \overline{r + s + t} > 0,$$

i. e., if 
$$r + s + t < 2q_3.$$

Also, (2) if 
$$\frac{2q_3 - \overline{r + s + t}}{q_2} < -2,$$

i. e. 
$$r + s + t > 2q_3 + 2q_2.$$

Consider, first, the line

$$r + s + t = 2q_3.$$

The equation is

$$q_1 \cos \theta_1 + q_2 \cos \theta_2 + q_3 \cos \theta_3 = q_1 + q_2 + q_3 - 2q_3$$

$$\text{or } q_1 (\cos \theta_1 - 1) + q_2 (\cos \theta_2 - 1) + q_3 (\cos \theta_3 + 1) = 0.$$

Putting  $\theta_1 = 0, \quad \theta_2 = \pi,$  we have

$$-2q_2 + q_3 (\cos \theta_3 + 1) = 0,$$

$$\text{or } \cos \theta_3 = \frac{2q_2}{q_3} - 1,$$

giving the direction of the tangent at  $q_3$  of the line.

[If  $q_2 = q_3, \theta_3 = 0$ , i. e., the line coincides with the axis.]

Again putting  $\theta_2 = 0, \quad \theta_3 = \pi,$

$$q_1 (\cos \theta_1 - 1) = 0.$$

$$\therefore \theta_1 = 0;$$

also  $\theta_1 = 0, \quad \theta_3 = \pi,$  gives  $\theta_2 = 0.$

Thus we see that the axis joining  $e_1$  and  $e_2$  is a portion of the line of force defined by  $r + s + t = 2q_3$ . And we conclude that this limiting line of force consists of a curved line through  $q_3$  and the axis joining  $q_1, q_2$ .

Taking next the line

$$r + s + t = 2q_3 + 2q_2,$$

we have

$$q_1 (\cos \theta_1 - 1) + q_2 (\cos \theta_2 - 1) + q_3 (\cos \theta_3 + 1) = 0.$$

Putting  $\theta_2 = 0, \quad \theta_3 = \pi,$

we have  $q_1 (\cos \theta_1 - 1) = -2q_2,$

$$\text{or } \cos \theta_1 = 1 - \frac{2q_2}{q_1},$$

giving the direction of the tangent to the line at  $q_1$ .

Again putting  $\theta_1 = 0, \quad \theta_2 = \pi,$

we have  $\theta_3 = \pi$

and if  $\theta_1 = 0, \quad \theta_3 = \pi,$  we have  $\theta_2 = 0,$

showing that the axis joining  $e_2, e_3$  is a portion of the line of force, defined by  $r + s + t = 2q_3 + 2q_2$ .

Hence this limiting line of force consists of a curved line through  $q_1$  and the axis joining  $q_2, q_3$ .

19. The above investigation may be summarized as follows :—

Starting with the line  $r+s+t = 2q_3$ , we have one series of lines, each of which consists of a branch issuing from  $q_3$  and going off to infinity and a closed branch joining  $q_1$  and  $q_2$  and another series, each consisting of a branch to infinity issuing from  $q_1$  and a closed branch joining  $q_2, q_3$ .

20. The line which separates the two sets will obviously be the line passing through a point of equilibrium.

Now the point of equilibrium is defined by distances

$$r_1, r_2, r_3 \text{ from } e_1, e_2, e_3,$$

$$\text{where } \frac{q_1(c_1 + c_2)}{r_1^3 c_2} = \frac{q_2}{r_2^3} = \frac{q_3(c_1 + c_2)}{r_3^3 c_1},$$

and  $c_1, c_2$  are the distances of  $e_1$  and  $e_3$  from  $e_2$ .

Also

$$(r_2^2 + c_1 c_2)(c_1 + c_2) = r_1^2 c_2 + r_2^2 c_1.$$

In figure V.,

$$q_1 = 15, \quad q_2 = 10, \quad q_3 = 10;$$

$$c_1 = 4, \quad c_2 = 2.$$

$$\text{This gives } r+s+t = 28.95.$$

The corresponding line of force is not therefore shown in the figure. And we conclude, further, that the lines  $r+s+t=20$  to 28 belong to the first set and 28 to 50 belong to the second set (art. 19).

In the figure IV. given at the end of Maxwell's Treatise, vol. i., we have

$$q_1 = 15, \quad q_2 = 12, \quad q_3 = 20.$$

$$c_1 = 9, \quad c_2 = 16.$$

$$\therefore r_1 = 15, \quad r_2 = 12, \quad r_3 = 20.$$

$$\cos \theta_1 = \frac{3}{5}, \quad \cos \theta_2 = 0, \quad \cos \theta_3 = -\frac{4}{5}.$$

$$\therefore r+s+t = q_1 + q_2 + q_3 - (q_1 \cos \theta_1 + \dots)$$

$$= 47 - 9 + 16$$

$$= 54 = \text{a whole number.}$$

If we therefore draw a diagram with these values of  $q_1, q_2$ , one of the lines so drawn will pass through the point of equilibrium, which will obviously be the point at which the two branches of this line of force will intersect.

21. As another example, we shall take the case of two equal and opposite charges in a uniform field.

The equation of a line of force is obviously

$$q(\cos \theta + \cos \theta') - \frac{y^2}{ap} = 2q - \overline{r+s+t},$$

being the intersection of the curves

$$q \cos \theta - \frac{y^2}{ap} = q - \overline{r+s},$$

and the radii of the circle of radius  $q$ , from the negative charge as centre, for which we have  $q \cos \theta' = q - t$ .

In figure VI. we have the first set of lines as in fig. IV. with their index numbers, and the intersections of these and the radii drawn from the negative charge at B, such that the final sum of the index numbers is constant, supply the points through which the lines of force are drawn.

We have taken the relative positions of the charges, to suit the case of an ideal magnet in a uniform magnetic field with the north pole directed to the north.

In order to suit this case,  $\theta$  and  $\theta'$  are measured from  $BA$  and  $AB$  produced.

22. Put  $\theta' = \pi$ ,  $y = 0$ .

We have  $\cos \theta = 3 - \frac{r+s+t}{q}$ .

$\therefore \theta$  is imaginary, if  $r+s+t < 2q$  or  $> 4q$ .

Similarly for  $\theta'$ .

The only lines of force issuing from either charge are therefore those which lie between  $2q$  and  $4q$ , and all these lines of force pass through both A and B.

23. Let  $r+s+t = 2q$ .

The equation is

$$\cos \theta + \cos \theta' - \frac{y^2}{qap} = 0.$$

This is obviously satisfied by

$$\theta = 0, \quad \theta' = \pi, \quad y = 0,$$

$$\text{and} \quad \theta = \pi, \quad \theta' = 0, \quad y = 0.$$

That is, the portions of the axis lying beyond A, B (on either side) are the two branches of the line of force in this case.

24. Again, let  $r + s + t = 4q$ .

We have  $\cos \theta + \cos \theta' - \frac{y^2}{qap} = -2$ .

Put  $\theta = \theta'$  and  $\tan \theta = -\frac{2y}{c}$ .

The values of  $\theta$  will define the points of intersection of the curve with the line perpendicular to AB, through its middle point.

We have  $2 \cos \theta - \frac{c^2}{4qap} \tan^2 \theta = -2$ .

Or  $2 (\cos \theta + 1) - \frac{c^2}{4qap} (\sec^2 \theta - 1) = 0$ .

Or  $\cos \theta + 1 = 0$ , *i. e.*  $\theta = \pi$ .

This corresponds to the portion of the axis lying between A and B. We have also

$$2 - \frac{c^2}{4qap} \cdot \frac{(1 - \cos \theta)}{\cos^2 \theta} = 0,$$

$$\text{i. e., } 2 \cos^2 \theta + \frac{c^2}{4qap} \cos \theta - \frac{c^2}{4qap} = 0.$$

Since  $\cos \theta$  is to be negative, this gives one admissible value of  $\cos \theta$ , showing there is another branch of the curve,

$$r + s + t = 4q.$$

25. It can also easily be shown that  $y$  is minimum, corresponding to this value of  $\cos \theta$ . The curve is therefore convex to the axis (AB) and obviously goes to infinity.

26. We conclude, therefore, that the line of force defined by  $r + s + t = 4q$ , consists also of two branches, viz., the portion of the axis between A and B and a branch going off to infinity. This branch, of which the minimum distance from the axis is finite, is convex to the axis.

27. Without further analysis but simply on the principle of continuity, we conclude :—

That the lines of force which converge to both A and B divide into two groups :—

(a) Starting with the portions of the axis lying beyond A and B, we have one group which consists of lines, each of

which has two branches, going to infinity, one issuing from A, the other from B.

(b) The other group consists of lines, each of which has a closed branch joining A and B, and a branch going off to infinity (both ways). This latter does not pass through either A or B, and is convex to AB.

The last line of this group consists of the limited line AB and an open branch at a finite distance from the axis.

28. Moreover, as the line infinity parallel to the axis is obviously a line of force, there must be a *third* group of lines, each consisting of a single branch going to infinity and lying beyond the last branch of the second group, which goes to infinity.

We have, accordingly, three groups of lines in this case.

29. Again, the line which passes through the point of equilibrium obviously separates the lines belonging to the first two groups.

If  $AB = 2c$ ,  $\rho$  = distance from A, B of the point of equilibrium, the line through the point of equilibrium should satisfy the condition

$$-\frac{c}{\rho} + \frac{c^3}{\rho^3} = 2 - \frac{r+s+t}{q}.$$

Also  $\rho^3 = qapc.$

In the case of fig. VI.,

$$q = 14, \quad p = 8a, \quad c = 3a.$$

$$\therefore \rho = 6.9 \text{ nearly,}$$

$$\text{and } r+s+t = 45.08 \text{ nearly.}$$

30. In the diagram, therefore, the final index number of the last line which has a finite branch should be 45. This is found to be the case. Moreover, each of the lines 28 to 44 consists of branches going from A and B to infinity while each of the lines 45 to 56 of a closed branch and another going to infinity.

Beyond the last branch of these latter, which goes to infinity, are lines, consisting of a single branch, likewise going off to infinity.



XIV. *On the Stresses in a Heavy Spherical Shell.*

By R. F. GWYTHER, M.A.\*

THIS represents a portion of a paper read before the Manchester Literary and Philosophical Society on the 7th of March. Stated shortly, the object of the paper is to show that the formal solution of the statical state of stress in a heavy body of an assigned shape is in certain cases determinable; that, in such a body, the determination of the statical state of stress should precede any investigation of the elastic stress in the body; and that, if the statical state of stress does not satisfy the conditions for being purely elastic, the equations for the elastic state of the body must be modified so as to conform with the statical conditions.

It is proposed to give here only the formal solution in a heavy spherical shell or bowl. The solution for a long heavy circular cylindrical tube lying horizontally is worked out in the paper, but a single instance is sufficient to gain the writer's object.

*Spherical Shell or Bowl or Dome.*

Consider the shell to be supported on a horizontal plane, all the circumstances being symmetrical about the vertical axis. Let the elements of stress at any point be ( $P, Q, R, S, T \sin \theta$  and  $U \sin \theta$ ), and the internal and external radii,  $a$  and  $b$ . Then the equation connecting  $S$  and  $T$  is an independent equation and, for our purpose, we may assume  $S$  and  $T$  to vanish.

The remaining equations are

$$r \frac{dP}{dr} + 2P - Q - R + 2Ux - (1-x^2) \frac{dU}{dx} = gprx, \quad . \quad . \quad (1)$$

$$r \frac{dU}{dr} + 3U - \frac{dQ}{dx} + (Q-R) \frac{x}{1-x^2} = -gpr, \quad . \quad . \quad (2)$$

where  $x$  stands for  $\cos \theta$ .

Without indicating here the reasons for the step, let us assume

$$Q = Ux + gpr \frac{x-\alpha}{1-x^2} + \frac{X}{r}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$R = Ux - (1-x^2) \frac{dU}{dx} - gprx - gpr \frac{x-\alpha}{1-x^2} + \frac{Y}{r}, \quad . \quad . \quad (4)$$

where the material ends with  $x=\alpha$  in case the shell is an open bowl. Otherwise  $\alpha=1$ .

\* Communicated by the Author.

Substituting in the general equations above, we obtain

$$\frac{d}{dr}(r^2P) = X + Y, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{d}{dr}(r^2U) = \frac{dX}{dx} - \frac{x}{1-x^2}(X-Y). \quad . \quad . \quad . \quad (6)$$

To make the conditions more precise, multiply equations (1), (2), (3), and (4) by  $r$ , and then integrate all the equations from  $r=a$  to  $r=b$  along the edges of the cone for which  $\cos \theta = x$ .

From (3) and (4) we obtain the equations for the equilibrium of that portion of the shell which lies within this cone, with the conditions

$$\int_a^b X dr = 0 \quad \text{and} \quad \int_a^b Y dr = 0 \quad . \quad . \quad . \quad (7)$$

From (5) we obtain

$$r^2P = \int_a^r (X + Y) dr,$$

remembering that  $P=0$  both when  $r=a$  and when  $r=b$ ; and from (6)

$$r^2U = \frac{d}{dx} \int_a^r X dr - \frac{x}{1-x^2} \int_a^r (X-Y) dr.$$

Since  $Q$  and  $U$  are both to vanish when  $x=\alpha$ , it is also necessary that  $X$  shall have the form

$$u \int_a^x v dx,$$

and that

$$\int_a^r uv dx + \frac{x}{1-x^2} \int_a^r Y dr$$

shall have the same analytical form. The formal solution is thus completed.

The expressions for  $Q$  and  $R$  involve essentially gravitational terms which are not dependent upon boundary conditions. If it is assumed that the stresses are purely elastic, as is assumed by all writers on that section of Elasticity usually referred to as "under bodily forces," these essential gravitational terms are excluded by the form of the consequent solution, which gives the stresses in zonal harmonics with coefficients of a definite kind when arranged in powers of  $r$ .

As the conclusion that the stresses between the parts of a heavy body are not purely elastic stresses, is contrary to the theory usually adopted, it appears desirable to mention that

the same gravitational terms were given by Rankine in the section on "domes" in his 'Applied Mechanics.' In this case, he professes to deal only with stresses other than those caused by cohesion or elastic reactions, whereas this paper includes general stresses to whatever physical causes they may be due.

If the conclusions are found to be well based, they may affect structural design and suggest lines of experiment on the strength of materials.

XV. *Note on the Internal Pressure of a Liquid.* By W. C. McC. LEWIS, M.A., D.Sc., *Physical Chemistry Laboratory, University College, London* \*.

RECENTLY (Phil. Mag. September 1910, p. 502, and *Kolloidzeitschrift*, vol. vii. p. 197, 1910) attention was drawn by the writer to the large discrepancies in the value of the internal pressure  $K$  of a liquid according as to whether we base calculation on van der Waals' equation ( $K = \frac{a}{v^2}$ ) or take Dupré's value which depends on the internal latent heat of vaporization of unit volume of the liquid. Thus, taking the case of water at ordinary temperature, the value of  $K$  from van der Waals' expression is 10,500–11,000 atmospheres, while the value given by Dupré's method is 23,900 atmospheres.

To account for the difference in the two sets of values, it was suggested that the density in the surface layer differed from that in the bulk of the liquid, it being necessary to assume that the average density in the surface is greater than that of the bulk. This entails as a consequence the supposition that the density passes through a maximum as we cross from liquid to vapour. On further consideration of the question, however, the conclusion has been come to that such a state of things could not represent a permanent equilibrium condition, and that therefore the hypothesis in question is no longer a tenable one. It seems possible that the discrepancies observed may be ascribed simply to the fact that molecular forces have a temperature coefficient. Dupré virtually assumed  $K$  independent of temperature. Van der Waals assumed (in the simple form of his equation) that  $K\rho^2$  is independent of temperature, where  $\rho$  denotes density. Neither of these is borne out by experience, though undoubtedly

\* Communicated by the Author.

van der Waals' is nearer the truth and would yield more accurate values of  $K$  provided an accurate value of  $a$  were obtained.

The simplest assumption we can make as regards the density changes in the surface layer is that there is a gradual decrease as we pass from the liquid to the vapour phase. This is the usually accepted view (*cf.* for example, G. Bakker, *Annalen der Physik*, xvii. p. 475, 1905). As regards liquid/liquid or liquid/solid interfaces, it is not known what may be the density distribution. It is not impossible that in such cases the density of one of the phases does pass through a maximum at the surface. Considering the case of the liquid/vapour interface, since the density decreases gradually it is extremely likely that  $K$  also decreases uniformly as we pass from liquid to vapour.

As regards the connexion between the true value of  $K$  (in the bulk of the liquid) and the latent heat of vaporization, we may proceed as follows.  $K$  denotes the internal work done per unit volume of the liquid against the molecular attracting forces when the molecules are supposed to be drawn apart until they are outside the range of their mutual attractions. In the process of vaporization, the internal energy change per unit volume of liquid, which is identical with the internal latent heat per unit volume, is not (necessarily) equal to the internal work done, which is measured by  $K$ . The equality would only hold good if  $K$  were independent of temperature, which is not the case. The true form of the Dupré relationship may possibly take the following shape,

$$K - \frac{L_i}{v} = T \left( \frac{\partial K}{\partial t} \right)_v,$$

where  $L_i$  = internal latent heat of vaporization per gram,

or

$$K = K_{\text{Dupré}} + T \left( \frac{\partial K}{\partial t} \right)_v.$$

In this it is assumed that  $K$  and  $L_i$  bear a relation to one another analogous to that between external work and heat change in other cases.

Since it is known that  $K$  decreases as temperature rises,  $K_{\text{Dupré}}$  can only represent at best an upper limit to the value of the internal pressure.

To obtain reliable values of  $K$ , it will be seen, requires some further assumption with respect to  $K$  in relation to  $T$ .

We can write the above equation in the form

$$l = -T^2 \frac{\partial}{\partial t} \left( \frac{K}{T} \right),$$

where  $l = \frac{L_i}{v}$ .

And if we write  $l$  as a linear function of the temperature we finally get some such equation as

$$K = a + bT \log T + cT,$$

where  $c$ , however, is an indeterminate integration constant. The problem resolves itself into one quite analogous to that which is being investigated by Nernst, viz. the connexion between heat change and chemical affinity.

It may be of interest to tabulate briefly the various explicit expressions which have been put forward for  $K$ , pointing out the assumptions upon which each rests.

(a) The Dupré relation (*Annales de Chimie et de Physique*, 1864 *seq.*, and 'Théorie mécanique de la Chaleur') already discussed, viz.

$$K = l.$$

The assumption is that  $K$  is independent of temperature.

(b) Dupré (*l. c.*) suggested another relation, viz.

$$K = -T \frac{\alpha_1}{\beta},$$

where  $\alpha_1$  is the coefficient of expansion of the liquid with temperature,  
and  $\beta$  „ „ compressibility of the liquid at constant temperature.

The above relation may be obtained as follows, assuming an equation of the van der Waals type, viz.

$$p = \frac{RT}{v-b} - K.$$

On differentiating with respect to temperature, assuming  $b$  is constant and further assuming as Dupré did that  $K$  is also independent of temperature, one obtains

$$\left( \frac{\partial p}{\partial t} \right)_v = \frac{p+K}{T} = \frac{K}{T}, \text{ neglecting } p \text{ compared with } K.$$

Now

$$\left(\frac{\partial v}{\partial t}\right)_p \left(\frac{\partial t}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T = -1;$$

$$\therefore K = -T \left(\frac{\partial v}{\partial t}\right)_p \left(\frac{\partial p}{\partial v}\right)_T = \frac{-\frac{T}{v} \left(\frac{\partial v}{\partial T}\right)_p}{\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T} = -T \frac{\alpha_1}{\beta}.$$

The assumption is the same as in the first relation.

(c) In the Dutch edition of the 'Continuity of the liquid and gaseous states' of van der Waals the following expression occurs :

$$K^2 = \frac{C_0(1 + \alpha t)}{v\beta},$$

where  $C_0$  = the volume of a given mass of vapour,

$v$  = the volume of the same mass of liquid.

$\alpha$  = the coefficient of gaseous expansion,

$\beta$  = the compressibility of the liquid.

This equation does not appear in the German edition nor in the English translation, its removal being probably due to the author. The relation is based on van der Waals' equation, and further it is assumed in its deduction that the

term  $\frac{2a}{v^3}$  for the liquid state is negligible compared with the term  $\frac{RT}{(v-b)^2}$ . In connexion with its application chiefly

to elementary substances (solid as well as liquid), cf. Traube, *Verhandlung d. deutsch. physik. Gesellschaft*, 1909.

(d) In the *Zeitschr. für phys. Chemie*, xl. p. 176, 1902, T. W. Richards writes the equation

$$K = C \frac{dt}{dv},$$

where  $C$  is the thermal capacity (say per gram molecule). Richards obtained this by considering that the heat which had to be added to a small volume element  $dv$  to raise the temperature  $dt$ , namely  $Cdt$ , was equivalent to the internal work done  $Kdv$ . He applies this to elementary substances, obtaining exceedingly large numerical values. The assumptions made are, first that  $K$  is independent of temperature, and second that it is practically independent of volume, which is far from the truth.

(e) Traube (*Zeitschr. für anorganische Chemie*, xxxiv. p. 416, 1903) takes up Richards' expression and shows that it yields values which are pretty exactly three times the

values obtained by applying van der Waals' equation to the same substances. (Traube considers van der Waals' equation applicable to the solid state. This is extremely doubtful, though the calculated values of  $K$  thereby obtained appear to be of the right order of magnitude.) Traube rewrites Richards' relation in the form

$$K = \frac{C}{3} \frac{dt}{dv}.$$

(*f*) C. Benedicks (*Zeitschr. für anorgan. Chemie*, xlvii. p. 455, 1905), in the course of an investigation as to whether van der Waals' equation may be applied to the solid state, and in which he points out that Traube's considerations are not conclusive, has deduced the following expression for  $K$ , viz.

$$K = \frac{a}{v^2} = \frac{R}{v} \left[ \frac{1}{\alpha_1} + 2T \right] = \frac{R}{v\alpha_1} \text{ approximately.}$$

(Benedicks writes  $3\beta$  for the coefficient of expansion of the liquid or solid with temperature, I have here denoted it by  $\alpha_1$ .)  $v$  denotes volume in the liquid state. The equation is based on that of van der Waals. It will be seen on comparing them that Richards' equation would only become identical with Benedicks' if  $C$  were put equal to  $R$ . For elementary bodies  $C$  is the atomic heat, a constant having the value 6 approx. (Dulong and Petit's law). The invalidity of Richards' formula is thus apparent. The formula of Benedicks is the most convenient one we have for calculating  $K$ —the values obtained being of course dependent upon the assumptions underlying van der Waals' equation.

It will be observed that the expressions for  $K$  rest on one or other of the assumptions, (1) that  $K$  itself is independent of temperature, or (2) that the  $a$  and  $b$  in van der Waals' equation are independent of temperature.

The relation

$$K - l = T \left( \frac{\partial K}{\partial T} \right)$$

is probably correct, but it does not allow calculation of  $K$  unless some new assumption be made with respect to  $K$  and  $T$ .

I take this opportunity to express my indebtedness to Prof. A. W. Porter, F.R.S., for helpful criticism and suggestions.

XVI. *Note on the Paper by Prof. E. Rutherford, F.R.S., and H. Geiger, Ph.D., on "The Probability Variations in Distribution of  $\alpha$  Particles."* By E. C. SNOW, M.A.\*

**I**N the Phil. Mag. for October last Prof. Rutherford and Dr. Geiger contributed a paper with the above title, a mathematical note by Mr. Bateman being appended. The latter showed that if  $x$  is the true average number of  $\alpha$  particles falling on a screen from a constant source in a given interval, the probability that  $n$   $\alpha$  particles are observed in the same interval is given by  $\frac{x^n}{n!} \cdot e^{-x}$  (p. 705). The figures

found by the experimenters were compared with those obtained from the above expression, and the conclusion reached was that "on the whole, theory and experiment are in excellent accord," but no numerical measure of the agreement was attempted.

As the distribution of the figures is of a general form often reached in many branches of statistics, it is of interest to compare the numbers given in the paper with those derived from fitting an ideal frequency curve to the experimental results, and also to obtain a measure of the "goodness of fit" of the latter with the theoretical values.

The theory of ideal frequency curves has been developed by Prof. Karl Pearson †, and the notation used here is that devised by him.

Taking the figures given by the experiments for  $\frac{1}{8}$  minute intervals (p. 701, last row but one) the following statistical constants are found :—

$$\mu_1 = 0.$$

$$\mu_2 = 3.6114.$$

$$\mu_3 = 3.3979.$$

$$\mu_4 = 45.9922.$$

$$\beta_1 = .2451.$$

$$\beta_2 = 3.5265.$$

A reference to Rhind's Tables ‡ shows that the distribution lies just within the area of Pearson's Type IV., but is quite close to Type V. The equation of the first of these is of the form

$$y = y_0(x^2 + a^2)^{-m} e^{-r \tan^{-1} x/a},$$

and of the second

$$y = y_0 x^{-p} \cdot e^{\gamma x}.$$

\* Communicated by the Author.

† Phil. Trans. vol. clxxxvi. A. pp. 343-414.

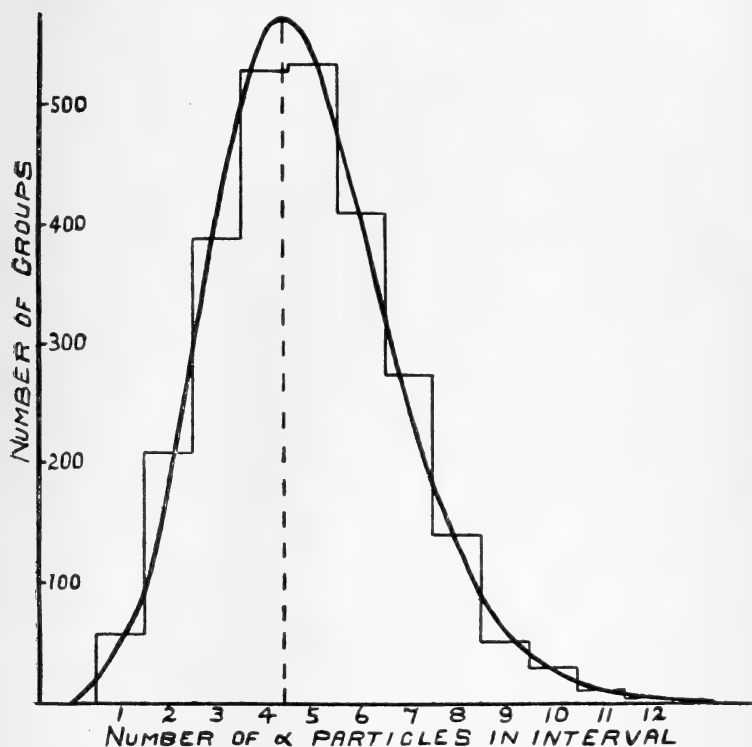
‡ 'Biometrika,' vol. vii. July and October 1909, p. 131.



As the latter is far more easy to draw than the former a curve of Type V. has been fitted to the data, the following being the extra constants involved :—

$$\begin{aligned} p &= 70.2582. & \log y_0 &= 116.1842. \\ \gamma &= +1063.8192. & \text{Origin} &= \text{mean} - 15.5852. \\ & & \text{Mode} &= \text{mean} - .4437, \end{aligned}$$

the skewness being .2335. The curve is shown in the diagram, the stepped figure giving the corresponding experimental frequencies. The areas of portions of the curve bounded by ordinates determined by the data are shown



below, the corresponding theoretical values and experimental numbers being also given. The last five observations are clubbed together as they could not accurately be measured separately by the planimeter.

Experimental values.	57	203	383	525	532	408	273	139	45	27	16
Theoretical values ...	54	210	407	525	508	394	254	140	68	29	21
Values from Curve...	57	216	399	553	533	391	251	123	49	24	12

For the "goodness of fit" \* of the experimental values with the curve we find  $\chi^2=9\cdot6270$  and  $P=\cdot474$ . For the theoretical values and the experimental values the figures are  $\chi^2=13\cdot9826$  and  $P=\cdot173$ . In the latter case, therefore, in one trial out of six a random sampling would lead to a system of numbers diverging more widely from the theory than do the actually observed figures. The fit may be considered fair. In the former case the corresponding probability is one in two, or three times as good. But this is obtained by the use of extra constants and must not be taken as controverting the authors' conclusions that "as far as the experiments have gone, there is no evidence that the variation in number of  $\alpha$  particles from interval to interval is greater than would be expected in a random distribution."

In the case of the  $\frac{1}{4}$  minute intervals the "goodness of fit" of the two rows of figures (the one obtained from experiment and the other from theory) given at the bottom of p. 703 of the paper can also be ascertained. Here  $\chi^2=14\cdot9953$  and  $P=\cdot31$ , the observations at the end of the range being clubbed together, as before.

Judging from the figures given, therefore, the agreement between theory and experiment in the case of the  $\frac{1}{4}$  minute intervals is better than in the  $\frac{1}{8}$  minute intervals, a conclusion opposite to that of the authors of the paper. This, however, can be accounted for by the very poor agreement between experiment and theory in the case of 8 particles per interval in the latter experiments. Here theory gave 68 while experiment only showed 45, and this discrepancy contributed no less than 7.78 to the total value (13.98) of  $\chi^2$ .

The ideal frequency distribution could also be obtained from the figures given for the  $\frac{1}{4}$  minute interval experiments. For these,  $\beta_1=\cdot2283$  and  $\beta_2=3\cdot6429$ , and the distribution has passed over into a true Type IV. curve, instead of being on the border-line between Type IV. and Type V. as in the case of the  $\frac{1}{8}$  minute interval experiment.

The Sir John Cass Technical Institute,  
London, E.C.  
March, 1911.

\* See Pearson, *Phil. Mag.* vol. 1. pp. 157-175, July 1900. Also "Tables for Testing the Goodness of Fit of Theory to Observation," W. Palin Elderton, 'Biometrika,' vol. i. pp. 155-163.

XVII. *The Transformation of the Actinium Emanation.**By H. GEIGER, Ph.D.\**

IT was first shown by H. L. Bronson† that the actinium emanation in breaking up emits two  $\alpha$  particles for each  $\alpha$  particle from the active deposit. This peculiarity was examined later by E. Marsden and myself‡, in order to settle whether the two  $\alpha$  particles are expelled together. By means of a double screen arrangement it was found that a large proportion of the scintillations, produced by the  $\alpha$  particles from the emanation, appeared as doublets, and the number of these apparent doublets was far greater than in the case of other radioactive substances. It was therefore concluded that either the decay of the emanation is connected with the simultaneous emission of two  $\alpha$  particles, or that the emanation is followed by another short-life  $\alpha$ -ray product of less than  $\frac{1}{10}$  second period.

In order to throw further light on this question I have investigated the ranges of the  $\alpha$  particles from the actinium emanation by the scintillation-method in the following way. A flat glass ring, about 1 mm. thick, was covered airtight on one side with a thin sheet of mica, whose stopping power was equivalent to 8 mm. of air. This ring could be pressed airtight against a plane metal plate, and in this way a shallow box was formed. The metal plate had two small holes which made it possible to circulate air carrying actinium emanation through the box.

In order to count the scintillations at different distances a zinc-sulphide screen was fixed to a microscope, which could be moved along a graduated scale. The scintillations were counted within the last 2 to 3 cms. of the range at intervals of 1 to 2 mm. The change in number which was due to the increase of distance was corrected for by multiplying each figure by the square of the distance at which the reading was taken.

Curve I. in fig. 1 shows the result obtained for the actinium emanation and its active deposit. The curve brings out clearly that three products of ranges 5.4, 5.7, and 6.5 cm. are present. The shortest range, viz. 5.4 cm., is obviously that of the  $\alpha$  particles from the active deposit which is generally given as 5.5 cm. To ascertain the correctness of this value an experiment was carried out for the active deposit alone, and the curve obtained is drawn on the same

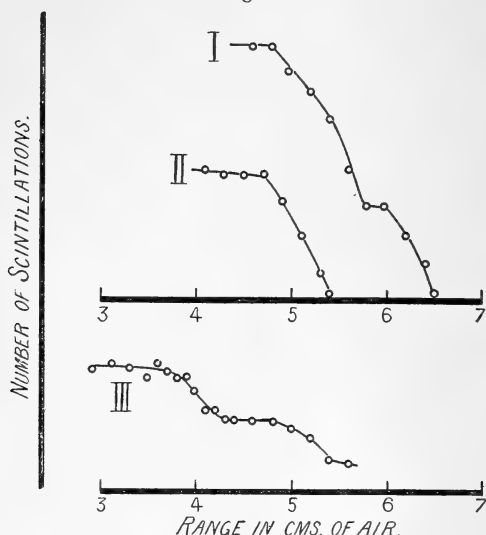
\* Communicated by Prof. E. Rutherford.

† H. L. Bronson, *Phil. Mag.* xvi. p. 291 (1908).

‡ H. Geiger and E. Marsden, *Phys. Zeitschr.* xi. p. 7 (1910).

scale in the figure [curve II.]. It follows, therefore, that the ranges 5.7 and 6.5 are both due to the  $\alpha$  particles from the actinium emanation.

Fig. 1.



It may be added here that with the above arrangement also a determination of the range of the  $\alpha$  particles from actinium X was carried out. This determination is somewhat complicated by the fact that it is impossible to obtain actinium X films free from emanation and active deposit, on account of the rapid growth of these substances. The thin actinium X film was placed inside the box described above, and a strong current of air was allowed to pass through it in order to reduce the effect from the emanation and the active deposit as much as possible. By carrying out countings in the same way as indicated above it was observed that  $\alpha$  particles of relatively short range [4.4 cm.] were present in addition to the  $\alpha$  rays from the emanation and the active deposit [curve III.].

In investigating the range of the  $\alpha$  particles from a film of actinium X, O. Hahn\* found a maximum range of 6.55 cm. Since it was not known at the time that two  $\alpha$  particles are given off from the actinium emanation, this long range was naturally, but incorrectly, ascribed to the  $\alpha$  particles from actinium X. The value found by Hahn for

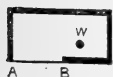
\* O. Hahn, *Phys. Zeitschr.* vii. p. 557 (1906).

the actinium emanation, namely 5.8 cm., is in good agreement with that given above.

The distinct difference in range of the  $\alpha$  particles from the actinium emanation makes it highly suggestive that the emanation consists of two successive products, which both emit  $\alpha$  rays. The 4 second product—the actual emanation—emits  $\alpha$  rays of range 5.7 cm. and the following short-lived product rays of a range of 6.5 cm.

An experiment which gives a still more direct evidence of the existence of this product, and also allows an approximate determination of its period, was suggested to me by Professor Rutherford, for which I am greatly indebted to him. The arrangement is shortly this. Actinium emanation was sucked through a metal tube of rectangular cross-section, as shown in fig. 2. The part AB of the tube, about 2.5 mm.

Fig. 2.



wide and 1 cm. long, was cut out and the opening covered by a thin sheet of mica. A wire W, insulated from the tube, and placed out of centre, as seen in the figure, could be charged negatively to any potential required.

If the short-lived product following the emanation is charged—as may reasonably be expected from an analogy of the corresponding products in the radium series—this product will be drawn to the wire W with a speed depending on the intensity of the electric field, as soon as it is formed. The screen, on which the scintillations were observed, was placed at such a distance from the mica window that only the  $\alpha$  particles of longest range could strike it. Any radiation from the wire W was screened off by the box.

Countings were taken alternately with and without the electric field. A very marked difference was found. The number of scintillations decreased to about  $\frac{1}{2}$  for a potential difference of about 30 volts, and to about  $\frac{1}{5}$  for a difference of 200 volts. More intense fields did not produce any increased effect, and this was probably due to the fact that some of the atoms of the short-lived product lost their charge, either by recombination or by contact with the walls, before the field had pulled them to the wire.

Since the migration constant of the radioactive atoms is the same as that of positive ions\*, it could be calculated that the period of the new substance is of the order of  $\frac{1}{500}$  second. This value can of course only be considered as a rough estimate; experiments by another method are at present in

\* J. Franck, *Verhandlgn. d. d. Phys. Ges.* xi. p. 397 (1909).

progress by Prof. Rutherford and myself, which, as it is hoped, will give an accurate value for the period.

In the case of thorium emanation, where the existence of a product of short life has already been pointed out in a previous note\*, similar effects have been observed, and will be communicated in a later paper.

Attention may be drawn to the fact that the values of the ranges obtained above throw new light on the relation—suggested by Prof. Rutherford † in 1907—between the period of the active substances and the ranges of the  $\alpha$  particles emitted by them. Such a relation has been found to hold more generally than was at first suspected. This will be discussed in a paper shortly to be published.

### *Results.*

It has been shown that the actinium emanation is complex, consisting of two products each of which emits  $\alpha$  rays. The first one—the emanation—with a period of 4 seconds emits  $\alpha$  rays of a range of 5.7 cm. The second product emits  $\alpha$  rays of range 6.5 cm., and has a period of the order of  $\frac{1}{500}$  of a second. The latter product carries a positive charge, and is probably a solid.

My thanks are due to Mr. J. M. Nuttall for the assistance he has given me in some of the experiments.

Physical Laboratory,  
Victoria University, Manchester.

## XVIII. *Charges on Ions in Gases.*

*To the Editors of the Philosophical Magazine.*

DEAR SIRS,—

**I**N a paper by Professor R. A. Millikan and Mr. Harvey Fletcher on the valency of gaseous ionization, which appeared in the June number of the *Philosophical Magazine*, some experiments on the determination of the charge on an ion are described, from which it is concluded that no ions with double charges are produced in a gas by primary or secondary Röntgen rays. The previous experiments by Professor Millikan, from which it was deduced that such double charges do exist, are said not to be so conclusive, and also all other investigations which show that positive ions

\* H. Geiger and E. Marsden, *l. c.*

† E. Rutherford, *Phil. Mag.* xiii. p. 110 (1907).

with double charges may be produced in the gas are criticised and said to be inconclusive and inconsistent.

I should like to point out that while admitting that it is difficult to reconcile all the experiments that have been made on this subject, still it appears to me to be obvious that if experimental results are to be accepted at all the balance of evidence is entirely in favour of supposing that such double charges exist, and that the difficulty of reconciling the results of different investigations lies probably in the fact that the exact circumstances under which a large proportion of positive ions with double charges are produced are not yet completely specified.

The first investigations by which the ratio of the charges on ions in liquids and gases were determined are those involving the comparison of the rate of diffusion with the velocity under an electric force from which a value of  $N \times e$  was deduced ( $N$  being the number of molecules per c.c. in a gas at atmospheric pressure and  $15^{\circ}$  C., and  $e$  the charge on the ion),  $N \times e$  being  $1.23 \times 10^{10}$  when  $e$  is the charge on a monovalent ion in a liquid electrolyte (Phil. Trans. A. 1899, vol. cxiii.). It was found that when the mean rate of diffusion of positive and negative ions was compared with the mean velocity under an electromotive force the values of  $N \times e$  for different gases were nearly the same as that for monovalent ions. The mean rates of diffusion and mean velocities under an electromotive force were compared in those determinations because at that time the velocities of the positive and negative ions were not known. Shortly afterwards the velocities of both positive and negative ions generated by Röntgen rays were determined by Zeleny (Phil. Trans. A. vol. cxcv. 1900), so that the values of  $N \times e$  for positive and negative ions could be deduced separately and the numbers obtained for positive ions were in seven cases out of eight distinctly larger for positive ions than for negative ions, the average excess being about 12 per cent. Professor Millikan attributes this to experimental error, as variations occur in determinations of  $N \times e$  in different gases. Such an explanation is not what would in an ordinary way be accepted as the most likely, since errors with different gases would be introduced, unless the gases were equally free from impurities, in determining the rate of diffusion and the velocity under an electric force.

It is not quite correct to say that in view of my recent experiments I revised my previous conclusions. When I found the value of  $N \times e$  produced by ions from a point discharge, I drew attention to the fact that the value of  $N \times e$

for positive ions was very large, that possibly some of the ions had double charges, and "in order to come to a definite conclusion with regard to the charges" further experiments would be required (Phil. Trans. vol. cxcv. 1900, p. 277).

The reason why a definite conclusion was not possible in the case of the point discharge was that the rate of diffusion could have been influenced by the presence of the nitric acid produced by the discharge, which would condense on the ions. I was aware at the time that ions with different rates of diffusion could easily be obtained in this case, with both positive and negative ions. The largest values of the rates of diffusion were therefore compared with the velocities, and the smallest values obtained for  $N \times e \times 10^{10}$  were much larger for positive ions than for negative ions, in the ratio 1.66 to 1.46.

The experiments with Röntgen rays do not involve so many difficulties. The velocities and rates of diffusion were found under very similar conditions, and the high values of the product  $N \times e$  obtained for positive ions cannot possibly be attributed to the cause suggested by Professor Millikan, namely, that the rate of diffusion is slow owing to the presence of positive ions of comparatively large mass with single charges. Such ions would affect the determination of the velocities by Zeleny's method to a great extent, as by that method it is the velocity of the slowest of the ions that would be measured, and if the mean rate of diffusion is compared with that velocity the number obtained for  $N \times e$  would be too small.

With regard to some experiments I have made recently (in which no error due to impurities can come in, as the values of  $N \times e$  can be found from a single experiment involving only the determination of the ratio of two charges), Professor Millikan suggests that the results are not consistent as a high degree of accuracy was not obtained by Mr. Haselfoot in some experiments of a similar kind, which he made with rays from a radioactive substance (C. E. Haselfoot, 'Proceedings of the Royal Society,' vol. lxxxii. 1909).

When I first published this method I pointed out that the results were reliable inasmuch as the same values of  $N \times e$  were obtained in a set of experiments with different forces, pressures, and intensities of ionization (Proc. Roy. Soc. vols. lxxx. & lxxxii. 1908). The actual numbers of all these experiments were not given, but it may be of interest to quote them. The observations were as follows:—



Pressure of Air in mm.	Force in volts per cm.	Intensity of ionization.	$N \times 10^{10}$ .
3	1.45	10	1.23
6	.98	8	1.23
6	1.47	16	1.25
6	1.96	13	1.15
6	2.96	17	1.27
12	1.00	8	1.20
12	.98	12	1.20
12	1.46	15	1.25
12	2.75	45	1.26
25*	1.47	33	1.30
25*	3.00	34	1.29

\* At 25 mm. pressure a correction of about 10 per cent. for self-repulsion has to be made which cannot be estimated very accurately.

The order of accuracy to be expected from the theory is not the same for all forces, so that a larger range of forces was not used. The accuracy is highest for forces of about 2 volts per centimetre when  $N \times e = 1.23 \times 10^{10}$ . It would be quite possible to alter the dimensions of the apparatus so as to give good results for practically any forces, but that was not considered necessary.

With the same apparatus the mean of the values obtained for positive ions was  $2.4 \times 10^{10}$ , the ions being produced by secondary rays from a very tarnished surface. When a bright surface was used and the air ionized by non-penetrating secondary rays the values of  $N \times e$  were  $1.26 \times 10^{10}$  and  $1.24 \times 10^{10}$  for positive and negative ions respectively. Afterwards by putting a thin layer of vaseline on the plate from which the secondary rays are produced the numbers found for positive and negative ions were  $2.06 \times 10^{10}$  and  $1.22 \times 10^{10}$  respectively.

Subsequently these experiments were made with hydrogen and carbonic acid, and the positive ions in these cases also were found to give different values for  $N \times e$  in the same way, while with negative ions the same value of  $N \times e$  was always obtained as was found for air.

It is not the nature of the gas obviously that determines whether or not large values of  $N \times e$  are obtained. The principal factor that has to be considered appears to be the kind of radiation that is used. The simplest explanation being that positive ions with single charges are produced when the rays consist of projected particles (which compose the non-penetrating secondary Röntgen rays), and that positive ions with double charges are produced by the direct action of the more penetrating secondary rays, which

resemble the X rays in not being deflected by a magnetic field.

This hypothesis seems to be in accordance with most of the experiments, but as there is a good deal of uncertainty as to the way in which gases are ionized by X-rays, it can only be considered as being adopted as a temporary explanation.

[Professor Millikan in quoting these experiments has inadvertently stated that ions with double charges are produced when the secondary rays come from a freshly cleaned surface.]

In Mr. Haselfoot's experiments which were made on the same lines as the above, the ions being produced by a radioactive substance, rather more experimental difficulties were encountered, and a value of  $N \times e = 1.26 \times 10^{10}$  was found for positive ions when a force of 2 volts per centimetre was used, and  $1.37 \times 10^{10}$  with a force of 4 volts per centimetre, thus giving a 9 per cent. difference, which according to Professor Millikan shows that the method is inconsistent. A reference to the curve for deducing the values of  $N \times e$  from the experiments shows that an error of 1 per cent. in the determination of the ratio of two charges gives rise to an error of about 2 per cent. in  $N \times e$  when a force of 4 volts per centimetre is used, and 1 per cent. when a force of 2 volts per centimetre is used, also in the previous case a larger experimental error is liable to come in. The probable error with 4 volts per centimetre is about 4 times as great as that with 2 volts per centimetre. Mr. Haselfoot calls attention to the probable inaccuracy of the number 1.37, and points out that 1.26 is the most reliable number.

The objection therefore that has been raised to the method is one that could be raised to any form of investigation,—namely that under some conditions the accuracy is not high.

What is of importance is that the accuracy is as high as can be expected from the theory as shown by the determinations with negative ions, with a suitable range of forces; and it ought to be possible to obtain the values of  $N \times e$  to an accuracy of 2 or 3 per cent. With the negative ions generated from molecules by Röntgen rays it has been shown that in all cases they have the same charge, which is confirmed by the experiments on the effects produced by collisions from which it is obvious that all negative ions must be precisely the same. It is extremely difficult to believe that the method fails when positive ions are investigated.

It may be pointed out that these experiments also brought to light a large effect due to moisture, which was subsequently confirmed when the velocities under an electromotive force

came to be determined. Also a similar effect in a much less degree was found in the previous experiments on the direct determination of the rates of diffusion at high pressures, which was subsequently found by Zeleny to affect the velocities. There is thus a considerable amount of evidence to show that the experiments on which the determinations of  $N \times e$  are based are reliable and consistent.

Experiments on the same principle as the previous work in which  $N \times e$  was found in gases at high pressure by determining the rate of diffusion and the velocity under an electric force have recently been made by J. Franck and W. Westphal\*, and they confirm to some extent the result obtained at low pressures, inasmuch as they find that the mean value of  $N \times e$  for positive ions produced by Röntgen rays is  $1.4 \times 10^{10}$ . According to Professor Millikan a larger number of positive ions ought to have been found than is indicated by this number if my conclusions are correct; and he suggests that the real reason why the number  $1.4 \times 10^{10}$  found for  $N \times e$  exceeds the theoretical number  $1.23 \times 10^{10}$  arises from an effect which makes the rate of diffusion too small. I have already explained why this suggestion cannot explain the high value  $1.4 \times 10^{10}$  obtained by this method. With regard to the number of ions with double charges that are to be expected, I cannot see that these experiments are inconsistent with those at low pressures, in which larger values of  $N \times e$  were obtained with positive ions. It must be remembered that when a beam of Röntgen rays traverses a gas there is a considerable secondary effect produced in the gas itself. It would be extremely difficult to separate the ions generated directly by the primary rays from those produced in the primary beam by the secondary rays, which consist of negative ions projected with a large velocity. The effect of these would not be so great in a small volume at low pressure, as they would reach the boundary before all their energy was spent in generating ions in the gas. It is not inconsistent with the determinations at low pressures that at high pressures there is a greater proportion of positive ions having single charges. Professor Millikan concludes from his experiments that the "greater part of the ionization of a gas by X-rays is due to the direct action by primary rays," which if it were true would make the above explanation untenable. It is extremely difficult to follow the reasoning which leads to this conclusion, but it is interesting in this connexion to note the results of experiments that have recently been made with gases

\* J. Franck & W. Westphal, *Ver. D. Phys. Ges.* Marz 5, 1909.

at high pressures (about atmospheric pressure) by Mr. R. T. Beatty\* and Mr. C. T. R. Wilson†. Mr. Beatty finds experimentally that when Röntgen rays pass through some gases a large part of the ionization is due to corpuscular rays, and that the fraction of the whole number of ions thus produced depends on the kind of primary rays that are used. Practically the same conclusion is arrived at by Mr. C. T. R. Wilson, in which he finds even with  $\gamma$ -rays that the ions in a gas are produced along fine lines traversing the gas in all directions—the tracks of  $\beta$  particles from the walls of the vessel.

The principal conclusions of the various experiments on these subjects are, it seems to me, much more in harmony than a superficial examination of the results would lead one to expect.

Professor Millikan's recent results, in which he found that none or very few positive ions with double charges were caught on the small drop that he had under observation, have led him to believe that no such positive ions are generated in the gas. It seems to me that, before such a definite conclusion can be arrived at, it would be necessary to know what proportion of the ions that are caught could be expected to be ions with double charges. If only nine or ten per cent. of the positive ions have double charges the question then arises, whether doubly charged ions are as likely to come into contact and adhere to the small drop as the smaller ions with a single positive charge. It would be rather difficult to decide what would happen with the different kinds of ions, but it is reasonable to suppose that doubly charged ions would have around them a larger group of molecules than the singly charged ions; and if, as Franck and Westphal found, their rate of diffusion is about half that of the smaller ions, their velocity of agitation would be proportionally small, so that they trace out a path through the molecules of the gas that would be half that of ions with single charges before they are brought up to the electrode. Under these circumstances any one of the doubly charged ions would be less likely than an ion with a single charge to strike a small object in the gas. Also the conditions under which ions with different masses would adhere to the drop are not necessarily the same. It is interesting to note in this connexion that the experiments have shown that negatives are caught more easily than positives.

\* "Ionization of Heavy Gases by X-Rays," Proceedings of Royal Society, A. vol. lxxxv. June 1911.

† "On a Method of making visible the Paths of Ionizing Particles through a Gas," Proceedings of Royal Society, A. vol. lxxxv. June 1911.

If the same kind of argument were used here as has been applied to the two kinds of positive ions, the experiments would have been said to show that there are more negatives than positives. It does not therefore appear to me that the evidence Professor Millikan has brought forward to show that all the positive ions in the gas have single atomic charges, is conclusive.

Yours truly,

JOHN S. TOWNSEND.

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XIX. *A Thermostat for Controlling the Temperature of a Room.* By The Earl of BERKELEY, F.R.S., and C. V. BURTON, D.Sc.\*

THE thermostat here described was designed for regulating the temperature of an interferometer room; a somewhat small cellar, which owing to its situation had to be heated by electricity. The current dealt with was 7 amperes at 100 volts, but the method to be described is capable of handling considerably larger currents, provided they are split up in parallel.

For our purpose it was essential that the temperature of the room should not vary by more than about half a degree for several days and nights on end.

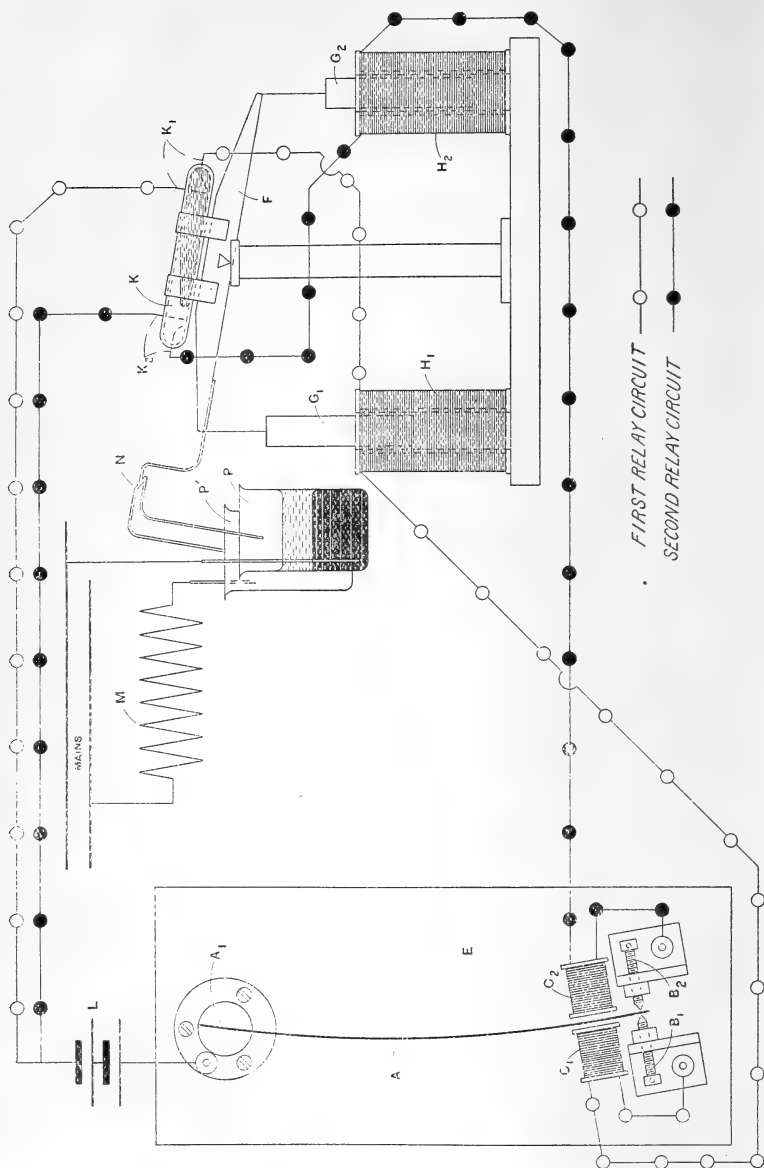
The sensitive member was a flat compound strip of brass and invar about a foot long† (we are indebted to Mr. A. Campbell for this suggestion), made by hard-soldering face to face a strip of brass and one of invar, and then rolling the compound strip to thin and harden it.

In the figure (p. 212), A is the brass-invar strip, whose upper end A<sub>1</sub> is fixed. B<sub>1</sub> and B<sub>2</sub> are platinum-tipped screws, one on each side of a platinum contact-piece rivetted into the lower end of the strip A. These screws are adjusted so that the freedom of motion of the strip is restricted to a small fraction of a millimetre. C<sub>1</sub> and C<sub>2</sub> are coreless solenoids, adjustably fixed to the board E, which carries the parts already named.

F is a wooden beam which can turn about a pivot by an amount limited by stops (not shown); G<sub>1</sub> and G<sub>2</sub> are short rods of soft iron, suspended from the ends of the beam F, co-axially with the solenoids H<sub>1</sub> and H<sub>2</sub>. K is a sealed glass tube fixed to the beam; it contains some mercury and is exhausted to a high vacuum. Two platinum wires are sealed

\* Communicated by the Authors.

† Later increased to 18 inches in length.



through each end of  $K$ .  $N$  is a fork of stout copper wire also fixed to the wooden beam  $F$ .

$P$  and  $P'$  are two small glass beakers containing mercury covered by Ragosin oil; the main heating current is made

and broken at these mercury surfaces, and the oil prevents undue sparking and oxidation.

M represents the electric heater, and L the two storage-cells of the relay circuit.

In the diagram the apparatus is represented at a moment when the room has become slightly overheated, and the heating circuit has been broken. As the air in the room cools, the strip A deflects towards the left, until it makes contact with the tip of the screw  $B_1$ . Starting from  $A_1$  we may trace the circuit through the strip A, the screw  $B_1$ , the solenoids  $C_1$  and  $H_1$ , the mercury contacts  $K_1$ , and the battery L, and then back to  $A_1$ . The solenoid  $H_1$  thus being energized, causes the armature  $G_1$  to be attracted, and so pulls the beam F over to the left; this causes the fork N to bridge across the two mercury vessels P and P', thus completing the heating circuit. At the same time the relay circuit is broken at  $K_1$  by the withdrawal of the mercury from the platinum wires  $K_1$ , and a second relay circuit, hitherto broken at  $K_2$ , has that breach made good by the mercury, and is ready to be completed so soon as a slight increase in the temperature of the room causes the strip to move towards the right and make contact with  $B_2$ . When this takes place the solenoids  $C_2$  and  $H_2$  are energized, the beam tips to the right thus breaking the heating circuit and also the second relay circuit at  $K_2$ .

It will be realized that the two positions of the strip A, in which it makes contact with  $B_1$  and  $B_2$  respectively, correspond to two finitely different temperatures. The difference between these temperatures, with the apparatus working at about  $15^\circ\text{C}$ ., is about  $0^\circ\cdot1\text{C}$ ., and corresponds to a linear freedom of motion of about  $0\cdot25\text{ mm}$ .

The reason for putting the solenoids  $C_1$  and  $C_2$  into the circuits is to remove all possibility of an incomplete or faltering contact between the strip and either of the contact points  $B_1$  and  $B_2$ ; as soon as contact begins, a feeble current is established in the relay circuit, and  $C_1$  or  $C_2$ , as the case may be, being slightly energized, attracts the invar of the strip A (the invar we used has sufficient permeability) and so increases the contact pressure, thus rapidly establishing full contact.

The mercury-tube K serves two purposes; when the beam tilts over, the mercury runs from one end of the glass tube to the other, thus preventing the beam from rebounding; at the same time the fact that the relay circuit is broken at the mercury contacts and not at the platinum contact points  $B_1$  or  $B_2$  helps to prevent the latter from getting "oxidized."

It may be mentioned that some slight trouble was experienced in adjusting the positions of the solenoids  $C_1$  and  $C_2$ . In the new thermostat, where the solenoids have been placed co-axially with the screws  $B_1$  and  $B_2$ , no difficulty has arisen.

Another slight difficulty that should be stated is that to get the best conditions of control it is necessary that the air in the room should be rapidly stirred by means of a fan; this, however, causes air currents to impinge upon the sensitive strip, thus making it vibrate. Wire gauze round, and a dash-pot at the end of\*, the strip (which is hung vertically), prevent the trouble. Neither the wire gauze nor the dash-pot is shown on the drawing.

In the course of the experiments with the interferometer it was found that, between the observations, while the observer was out of the room, it was advantageous to replace him by a heated dummy, thus keeping the conditions as constant as possible.

The following results give the temperatures of the air inside the interferometer case. During the hour from 10.5 to 11.5 A.M. the observer replaced the dummy, and was seated within 1 foot of the case :—

Time.	Temp.	Time.	Temp.	Time.	Temp.
9.0 A.M.	19°15 C.	10.20 A.M.	19°16+	11.20 A.M.	19°16+
9.31	19°15+	10.35	19°16—	11.35	19°16+
10.5	19°16—	10.50	19°16	11.50	19°16+
10.20	19°16+	11.5	19°16	12.15	19°17

XX. *On the Origin of Spectra.* By FRANK HORTON, D.Sc., M.A., Fellow of St. John's College, Cambridge†.

IN a paper recently communicated to the Royal Society‡, the author has given an account of some experiments with mercury vacuum-tubes which show that mercury is capable of giving several distinct line spectra when rendered luminous by an electrical discharge. The particular spectrum appearing in any given case depends upon the energy of the discharge in relation to the mass of vapour through which it passes. The spectrum most easily produced consists of five bright lines, but as the energy of the discharge is increased

\* Possibly improved results could be obtained if the contact points were placed under oil.

† Communicated by the Author.

‡ Roy. Soc. Proc. 1911.



other spectra, recorded in the paper, make their appearance in turn. Reasons can be given for thinking that these more complicated spectra are due to the formation of definite electronic systems, which are practically unstable new substances formed from the normal mercury atoms by the passage of the discharge, and that they are not due merely to different modes of vibration of the electrons in some one system, such, for instance, as the mercury atom.

In many respects mercury appears to be an ideal substance to use for investigating the origin of spectra. Its vapour is monatomic and can be rendered luminous in several ways: by the electric arc, or spark, or by the vacuum-tube discharge. This latter may be produced (*a*) by an induction-coil discharge with variable capacity and self-induction in the circuit, (*b*) by means of the low potential discharge from a glowing lime cathode, (*c*) by electromagnetic induction in the electrodeless ring discharge. Under these different conditions a continuous spectrum, a band spectrum, and spectra with different numbers of bright lines may be obtained.

As the result of a careful investigation of the spectrum of mercury, Stark \* has concluded that mercury possesses two distinct line spectra, that given by the arc *in vacuo* and that given by a vacuum-tube discharge. These he identifies as being due to monovalent and to divalent atoms—atoms which have lost one and two electrons respectively. Stark's views on the origin of spectra may briefly be summarized as follows:

(1) Continuous spectra are due to freely moving electrons, the accelerations of which are continually being changed.

(2) Line spectra are due to the vibrations of the electrons contained in the positive ions, all the lines of a series being due to the same source; but a single positive ion may be the source of several series of lines at the same time.

(3) Band spectra are due to electrically neutral bodies, and are formed in the act of combination of the negative electron with the positive ion.

In addition to the conclusion that mercury should have two distinct line spectra, Stark also holds that there should be two distinct band spectra, one formed by the combination of a divalent positive ion with a negative electron to form a monovalent ion, the other produced when the monovalent ion unites with another electron to form a neutral atom.

These views of Stark have been criticised by W. Wien †, who, from observations of the effect of a magnetic field on

\* Stark, *Ann. d. Phys.* xvi. p. 490 (1905).

† Wien, *Ann. d. Phys.* xxx. p. 349 (1909).

canal-rays formed in various vapours and gases, has come to the conclusion that the carriers responsible for the line spectra are neutral atoms, and that the vibrations producing the luminosity are caused by the recombination of negative electrons with the positive "remainder atoms." This is the view which is, I think, supported by the result of my recent observations of the spectra of mercury under different electrical conditions. In the paper already referred to five distinct line spectra are recorded. These, I think, are due to the recombinations of remainder atoms of different "electric atomic weights" with the appropriate number of negative electrons to form neutral systems. These systems are probably not similar in all respects to the atoms of the unionized gas, but are less stable arrangements of positive ions with one or more negative electrons revolving round them—each system being electrically neutral. The periods of these systems would depend upon the arrangement of the electrons around the central positive ion. There would be different equilibrium positions and consequently several possible periods for any one system. These would be affected by a magnetic field in such a way as to account for the Zeeman effect.

The fact that compounds always give banded spectra would seem to indicate that these are due, not to electrons, but to the vibrations of larger bodies. Since they produce light of the same wave-length, these larger bodies must be under the influence of more intense forces, which suggests that they are not separate atoms, but systems of atomic dimensions vibrating inside the molecule itself. On these views of the origin of line and of band spectra we should expect that a gas or vapour consisting solely of molecules in a normal condition would give a band spectrum, a conclusion which is borne out by the fact that the absorption spectra of such gases always consist of bands. In the case of the vapours of the alkali metals, which give line spectra, we have molecules which are not in a "normal" condition, as is shown by the abnormal conductivity of these vapours.

To obtain the emission spectrum of a gas we have to render it luminous by an electric discharge, and the effect of this is to ionize the molecules and to alter the composition of the gas. Electrons are set free; positive ions are produced, and by the collisions of these, vibrating systems are formed which radiate the energy of the spectrum lines. This difference in the composition of the gas is clearly shown by the experiments of Ladenburg\* and of Pflüger† on the absorption of light

\* Ladenburg, *Deutsch. Phys. Gesell. Verh.* x, 14, p. 550 (1908).

† Pflüger, *Ann. d. Phys.* xxiv, 3, p. 515 (1907).

by hydrogen. These experimenters could get no absorption of light by the gas in the normal condition, but found distinct absorption of the red and other lines when light was passed through a long tube containing the gas at a pressure of a few centimetres, conveying an electric current. Evidently these lines are due to something which does not exist in the gas in the normal state, but is produced in it by the passage of the discharge. Similar results have been obtained with mercury vapour. The absorption of this was first investigated by Lockyer \*, and later by Strutt † ; neither observer was able to obtain any absorption in the luminous spectrum, but more recently Wood ‡ has shown that there is absorption in the ultra-violet. That ionized mercury vapour does produce absorption has been demonstrated by Küch and Retschinsky §, and also by Pflüger ||. The method consists in having two mercury arc lamps placed one behind the other, and in measuring the percentage absorption of the light from the first lamp in passing through the second, in the case of certain definite lines of the spectrum. The results showed that ionized mercury vapour possesses the power of absorbing those rays which it emits, whereas the vapour in the normal condition produces no absorption.

We thus see that ionized gases and vapours contain electronic systems which are not present in them in the normal state. These systems are the "molecules" of new substances formed from the original gas or vapour by the passage of the electric discharge. I call them "new substances" because it is probable that they possess chemical properties different from those of the original substance. A simple experiment due to Dr. H. Brereton Baker ¶ shows that ionized mercury vapour has at least one different chemical property from mercury vapour in the ordinary atomic condition ; for if oxygen is allowed to enter a mercury lamp immediately after the current has been cut off, it is found that a considerable quantity of mercuric oxide is formed, although the temperature is much lower than that at which mercury vapour in a normal condition combines with oxygen.

The recent experiments of Sir J. J. Thomson \*\* have shown

\* Lockyer, Roy. Soc. Proc. xxii. p. 374 (1874).

† Strutt, Phil. Mag. vi. p. 76 (1903).

‡ Wood, Astrophys. Journ. xxvi. p. 41 (1907).

§ Küch and Retschinsky, *Ann. d. Phys.* xxii. p. 852 (1907).

|| Pflüger, *Ann. d. Phys.* xxiv. 3, p. 515 (1907).

¶ Baker, *Nature*, lxxxiv. p. 388 (1910).

\*\* Thomson, Phil. Mag. xxi. p. 225 (1911).

that the carriers of positive electricity in a vacuum-tube are often more complex than the original gas or vapour through which the discharge is passing. Thus in the case of oxygen gas, carriers of positive electricity with "electric atomic weights" 8, 16, 32, 48, and 96 have been discovered. The first of these corresponds to the atom of oxygen with two positive charges,  $O_{++}$ ; the second to the atom with one positive charge,  $O_+$ ; the third to the oxygen molecule  $(O_2)_+$ ; the fourth to the molecule of ozone  $(O_3)_+$ ; and the fifth to  $(O_6)_+$ . The vibrations of each of these positive ions may give rise to luminous radiation, or this may come from neutral systems formed by collisions with electrons. The vibrations of these neutral systems would, on Wien's theory, give rise to spectrum lines. On the other hand, we should expect that if the vibrations of the carriers of greater "electric atomic weight" give rise to luminous radiation, its spectrum would consist of bands, and it is well known that bands, especially in the green, are the characteristic feature of the spectrum of oxygen at low pressures. At higher pressures the bands are not so marked, which is the result to be expected, for the more frequent collisions would tend to prevent the formation of complicated molecules.

In the case of mercury vapour Professor Thomson has detected positive carriers with electric atomic weights of 800, 200, 100, and 66, corresponding to  $(Hg_4)_+$ ,  $Hg_+$ ,  $Hg_{++}$ , and  $Hg_{+++}$ , respectively. As in the case of oxygen, it seems probable that it is the vibrations of large atomic aggregates such as  $(Hg_4)_+$  which are the origin of the band spectrum observed by Eder and Valenta\*, Huff†, and others. If Wien's view is correct, it is the carriers of smaller mass, which, by their collisions with free electrons, form the systems producing the various spectrum lines, and the different line spectra which the author has observed are probably due to the different neutral systems formed. More energy would be required for the formation of a positive ion with three charges than for the formation of an ion with two charges or with unit charge, and so the neutral systems containing positive ions with the smallest electric atomic weights would be the last to be formed as the energy of the discharge is increased. Since these systems contain the largest number of oscillating electrons, they are capable of producing the greatest number of spectrum lines; so that we should expect the spectrum with most lines to be formed when the discharge

\* Eder and Valenta, *Denkschrift. Wien Akad.* lxi. p. 401 (1894).

† Huff, *Astrophys. Journ.* xii. p. 103 (1900).

contains the greatest amount of energy. This is in agreement with the experimental results, for the "many-lined spectrum" of mercury is obtained when a heavy discharge with capacity in the circuit is passed through the vapour at a low pressure.

Since a definite minimum amount of energy may be expected to be required for the production of any one form of positive ion, it follows that the corresponding neutral system, and the lines to which it gives rise, will appear when the energy is increased up to that value; and it is this which makes it possible to obtain several distinct spectra with quite definite changes from one to the other as the electrical conditions are gradually altered. The new spectrum is not at its best when first visible, but the new lines get brighter as further change in the conditions of the discharge increases the number of systems emitting them. If the conditions of the discharge are such as to form several types of radiating centres at the same time, the spectrum contains the lines due to all of them. The "many-lined spectrum" observed by the author contained all the lines of the other spectra with the exception of five in the red and orange regions which were sometimes seen, but were not visible when the spectrum was at its best.

## XXI. *Notices respecting New Books.*

RECENT publications of the *U.S. Coast and Geodetic Survey* include "Results of Observations made at the . . . Magnetic Observatory at Cheltenham, Maryland, 1907 & 1908, by DANIEL L. HAZARD," and "Arctic Tides by ROLLIN A. HARRIS" (Washington, 1911).

THE former publication follows the same general lines as earlier volumes of the series, but the copies of disturbed magnetic curves are allowed a time-scale of 15 mm. to the hour instead of 9 mm. as previously. This is a marked improvement, as it allows details to be followed with much greater ease and accuracy.

The second volume deals in the first instance with tidal observations along the north coast of Grant Land and Greenland made by the Peary Arctic Expedition of 1908-9, but collects for comparison practically all available results relating to tides in high northern latitudes. A table is given of the harmonic tidal constants at all stations north of  $60^\circ$  for which the author could find data. There is a discussion of the phenomena and some criticism of Dr. Nansen's views. The volume merits the attention of all interested in tidal analysis.

XXII. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

[Continued from vol. xxi. p. 696.]

December 21st, 1910.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

THE following communication was read:—

‘The Relationship of the Permian to the Trias in Nottinghamshire.’ By Robert Lionel Sherlock, B.Sc., A.R.C.Sc., F.G.S.

In South Nottinghamshire the Permo-Trias consists of the following divisions:—

KEUPER .....	{ Marls. Waterstones.
BUNTER .....	{ Pebble Beds. Lower Mottled Sandstone.
PERMIAN .....	{ Middle Marl. Lower Magnesian Limestone. Marl Slates and Breccia locally.

The conformability or unconformability of the Bunter to the Permian has been much discussed, but it is generally considered that there is a small unconformity between them. The evidence for this is the appearance of an Upper Magnesian Limestone, and locally an Upper Marl, between the Middle Marl and the Bunter, as the beds are followed northwards, so that the Bunter appears to overlap the Permian divisions from north to south.

In this paper, a section on the Great Central Railway, near Annesley, is described, which shows a gradual passage from the Middle Marl into the Lower Mottled Sandstone. Detailed mapping on the 6-inch scale between Nottingham and Market Warsop has confirmed this conclusion.

From Nottingham to Mansfield the Middle Marl retains a uniform character and thickness, but at Mansfield it is apparently absent, and the Bunter has been thought to overlap it and rest directly on the Lower Magnesian Limestone. At the same place the limestone becomes very sandy, forming the Mansfield Sandstone. It is shown that these two phenomena can be best explained by supposing that a river deposited a sandbar at Mansfield during Permian times, so that the limestone was replaced by sandstone, as was also, later, the Middle Marl. The sandy representative of the Middle Marl has been mistaken for Bunter, and so given rise to the appearance of an overlap.

North of Mansfield the Middle Marl becomes normal again. Near Cuckney the Upper Magnesian Limestone first appears as a very thin bed, and evidence is brought forward to show that the limestone arises as thin lenticular bands in the Passage-Bed, which develop northwards into a definite bed. In precisely the same way,

sandstone lenticles in the marl in South Nottinghamshire develop into a definite bed of sandrock, called the Lower Mottled Sandstone, At first, a thin Upper Magnesian Limestone is found below a diminished representative of the Lower Mottled Sandstone; but, on following the outcrop northwards, the Upper Limestone is seen to grow in importance and the Lower Mottled to diminish, until, in South Yorkshire, it is not found.

The Permian rocks continue to increase in thickness and the Bunter to diminish, until the Pebble Beds also become unrecognizable, in North Yorkshire. Also the Middle Marl now fails, and a thick mass of limestone remains to represent the Permian. The Keuper Waterstones persist throughout, and seem to be slightly unconformable to the Bunter.

From these considerations it is believed that the Upper Magnesian Limestone and Upper Marl of the northern part of the outcrop are the time equivalents of the Bunter of South Nottinghamshire, the one being deposited in an inland sea, comparable with the Caspian, the other along the coast-line, which was slowly moving northwards.

The palæontology of the Upper Magnesian Limestone is discussed, and the evidence derivable from the fossils is shown to be not unfavourable to the above view.

### XXIII. *Intelligence and Miscellaneous Articles.*

#### ON THE EQUATION OF CONTINUITY OF THE LIQUID AND GASEOUS STATES OF MATTER.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

Moscow, May 11th, 1911.

IN the article "On the Equation of Continuity of the Liquid and Gaseous States of Matter," printed in the *Phil. Mag.* October 1910, Mr. Kleeman gives an empirical relation between the internal latent heat of evaporation  $L$  and the densities of a substance  $\rho_1$  and  $\rho_2$  resp. in the liquid and gaseous state. The relation consists in that the function

$$\frac{L}{\rho_1^2 - \rho_2^2}$$

is approximately constant for each substance (p. 678 *sqq.*).

I venture to point out that this relation was found out by me in 1904, and published in the *Annalen der Physik*, vol. xiv. p. 305 *sqq.*

I beg to remain,

Yours truly,

A. BATSCHINSKI.

Privat-docent of the University of Moscow.

## PRINCIPLE OF RELATIVITY.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

Antibes, May 16th, 1911.

Mr. R. C. Tolman, in an article which appeared in the *Philosophical Magazine* (vol. xxi. March 1911), points out how the principle of relativity conduces to the expression of the force to which an electric charge in an electromagnetic field is submitted.

I laid before the Congress of Radiology and Electricity of Brussels (September 1910) the following consequences of the principle of relativity:—

A charge in uniform motion creates, besides its electrostatic field, an induced field (corresponding to induction by the motion of a current of constant intensity)—and a magnetic field.

A charge in uniform motion in a magnetic field is subjected, by the fact of its motion, to the force of Hall-Lorentz normal to the speed and to the field, proportional to their product and to the sine of their angle, a result Mr. Tolman has just established.

The volume of the Communications of the Congress has not yet appeared, but a summary of my results is inserted in *Le Radium* (August number, 1910).

I should be very much obliged to you, Gentlemen, if you would be good enough to accord my letter a place in the next number of the *Philosophical Magazine*.

Believe me,

Yours faithfully,

E. M. LÉMERAY.

## THE MODE OF IONIZATION BY X-RAYS.

The University, Leeds.

June 6, 1911.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

In the June number of your Magazine Prof. Millikan and Mr. Fletcher state (p. 761) that an oil drop which they were observing caught very few negative ions when placed a few millimetres (as I judge from their diagram) to one side of a stream of X-rays passing through air at atmospheric pressure; the imposed electric field being such as to urge negative ions made in the stream to move away from the drop. This, the authors say, “shows conclusively that the greater part of the ionization of a gas by X-rays is due to the direct action of the primary rays.”

The experiment does indeed show that very little of the ionization was due to secondary rays which penetrated the air so far from the primary stream as to get at the other side of the drop: this was to be expected. But it does not clash at all with a certain consequence\* of the corpuscular theory of X-rays, which is, that

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\* Bragg, “Consequences of the corpuscular hypothesis of the  $\gamma$  and X-rays,” *Phil. Mag.* Sept. 1910.



ionization by X-rays is effected indirectly by the cathode rays which spring from the X-rays, and that there is *no* direct ionizing action of the primary rays. The cathode rays have a range in air of two or three millimetres at the outside, and only the more penetrating have as much as that. All but a very small fraction of the ionization is to be found less than a millimetre away from the primary stream of X-rays.

I am, Yours &c.,

W. H. BRAGG.

CORRECTION TO DR. W. F. G. SWANN'S PAPER ON THE "LONGITUDINAL AND TRANSVERSE MASS OF AN ELECTRON." (Phil. Mag. June 1911.)

The expression  $\frac{\partial U}{\partial t} = \frac{\partial U}{\partial p} \cdot \frac{\partial p}{\partial t}$  given in the first equation in the paper should really be

$$\frac{\partial U}{\partial t} = \frac{\partial U}{\partial p} \frac{\partial p}{\partial t} + \frac{\partial U}{\partial q} \frac{\partial q}{\partial t} + \frac{\partial U}{\partial r} \frac{\partial r}{\partial t},$$

with similar expressions for  $\frac{\partial V}{\partial t}$  and  $\frac{\partial W}{\partial t}$ . The terms omitted in the paper, however, obviously always vanish for the case  $p=v$ ,  $q=r=0$ , which is the one treated in the paper, for the  $q$  and  $r$  derivatives of  $U$  vanish from symmetry, and the omitted derivatives of  $V$  and  $W$  vanish, because they involve either  $q$  or  $r$  as a factor. Thus the remainder of the argument in the paper is exact.

W. F. G. SWANN.

#### ANNUAL TABLES OF CONSTANTS AND NUMERICAL DATA CHEMICAL, PHYSICAL, AND TECHNOLOGICAL.

INTERNATIONAL COMMISSION OF PUBLICATION

*Appointed by the VIIth International Congress of Applied Chemistry  
in London, 2nd June, 1909.*

At the International Congress of Applied Chemistry held in London in 1909 an International Commission was appointed for the purpose of compiling and publishing Annual Tables of Constants and Numerical Data; and this Commission was subsequently accorded the patronage of the Association of Academies at the meeting of that body held in Rome in 1910 ('Nature,' May 26, 1910, p. 371).

According to the programme drawn up by the Commission the Tables published in any one year are intended to contain all the numerical data likely to be of interest in connexion with Chemistry, Physics, and allied Sciences, pure and applied, to be found in the literature published during the previous year. The data are to

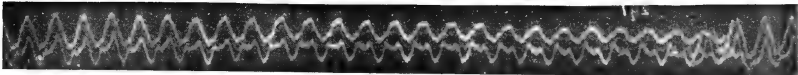
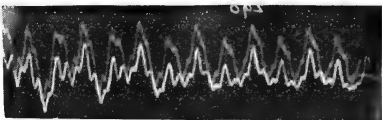
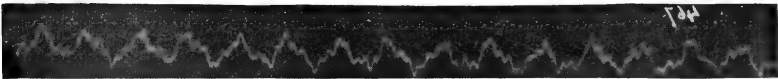
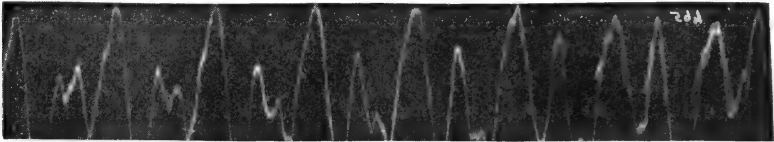
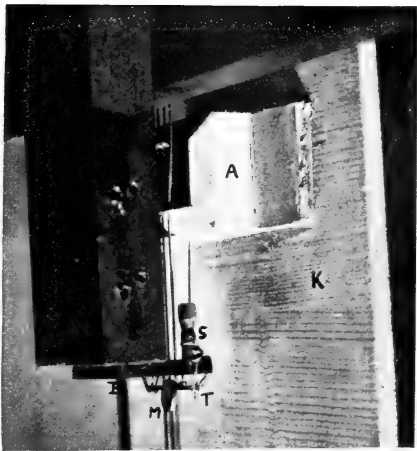
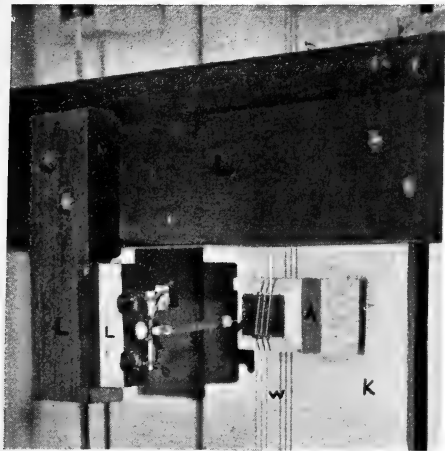
be accompanied by full bibliographic references. This programme has now (May 1911) so far matured, that portions of the volume for 1910 are already in the press, while the manuscript of the remaining portions is approaching completion.

Owing to the immense volume of scientific and technical literature which is continually being produced, the difficulties in the way of finding out whether any given measurement has been made or not are increasing year by year. Existing systems of indexing and abstracting offer only limited help, since a large number of measurements are made in the course of researches to which they are purely subsidiary, so that their existence cannot be inferred from the titles and subtitles of the papers in which they are recorded. Also Tables which appear only at long intervals such as those of Landolt and Börnstein, can of necessity cover only a small part of the ground; and moreover, in most cases they are hampered by the limitations of private enterprise. The Annual Tables should therefore fill a serious gap which has hitherto existed in the systematic indexing of scientific and technical results.

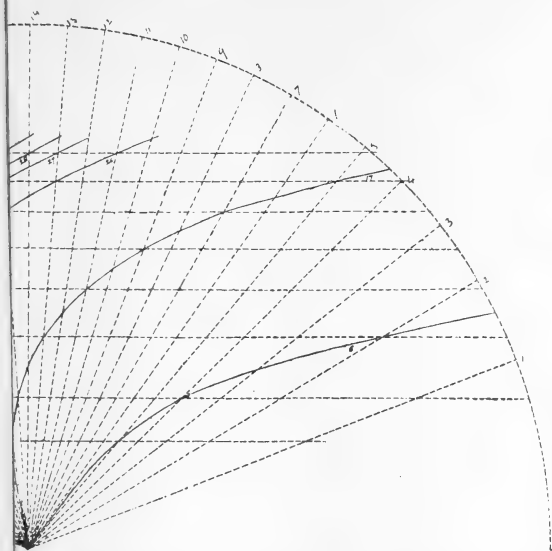
It is hoped that ultimately the enterprise may become self-supporting; but obviously this cannot be the case for some time to come. The Commission has been greatly assisted by grants from various Societies, for example, in this Country, from the British Association, Chemical Society, Faraday Society, Royal Dublin Society, Royal Irish Academy, Royal Society of Edinburgh, and the Society of Chemical Industry. Donations have also been received from a few private persons, notably from the Rt. Hon. the Earl of Berkeley, F.R.S. The financial position is, however, still far from satisfactory; and further help from Societies and private donors is urgently needed. In this connexion it may be mentioned that neither the General Secretary nor the Members of the Commission receive payment for their services, except in so far as they may perform actual compiling or abstracting.

The organization of the Commission is sufficiently complete to deal effectively with the periodical literature, but it happens occasionally that data are published only in non-periodical publications, such as books or monographs; and such data may easily be overlooked. Accordingly, in order that the Annual Tables may be as complete as possible, the authors of such books, monographs, &c., are requested to communicate with one or other of the members of the Commission. In cases where the data are numerous, specimen copies or corrected proofs of the tables containing the data would be very acceptable.

The members of the International Commission for the United Kingdom are: Dr. Alex. Findlay, The University, Edgbaston, Birmingham; Dr. R. T. Glazebrook, C.B., F.R.S., The National Physical Laboratory, Teddington, Middlesex; and Dr. N. T. M. Wilsmore, University College, Gower Street, London, W.C. The General Secretary is Dr. Charles Marie, 98 Rue du Cherche-Midi, Paris VI.









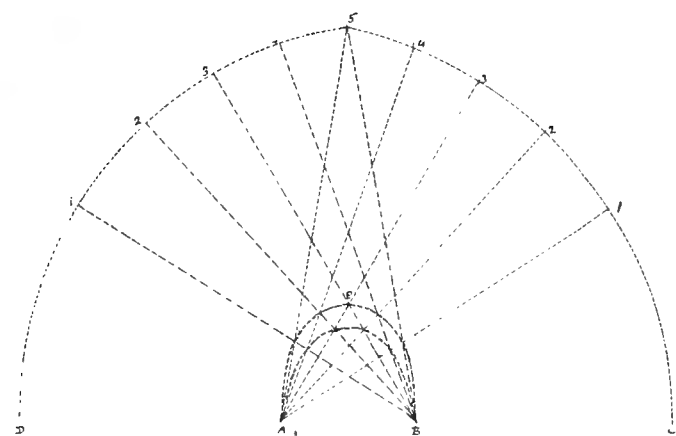


FIG. I.

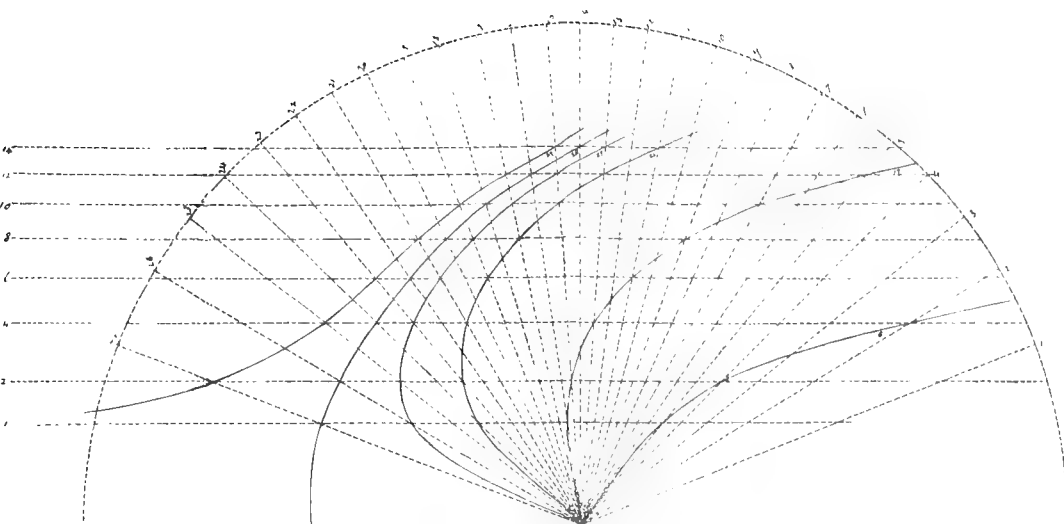


FIG. IV.

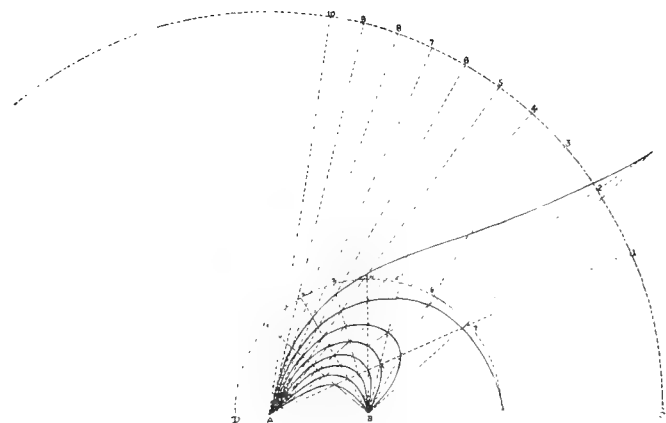


FIG. II.

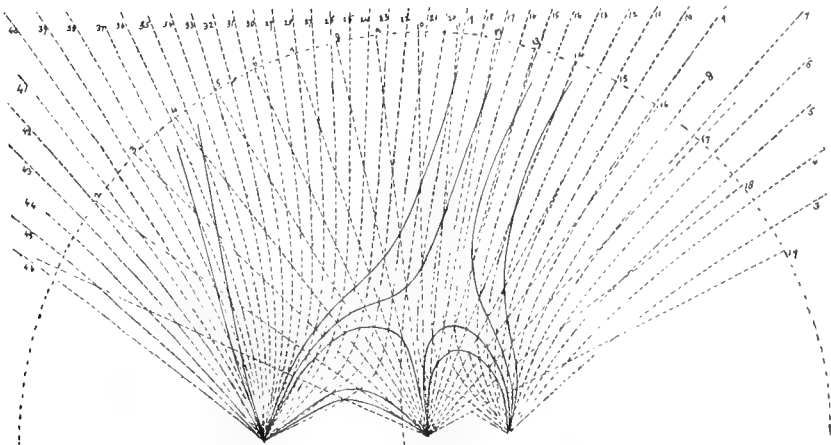


FIG. V.

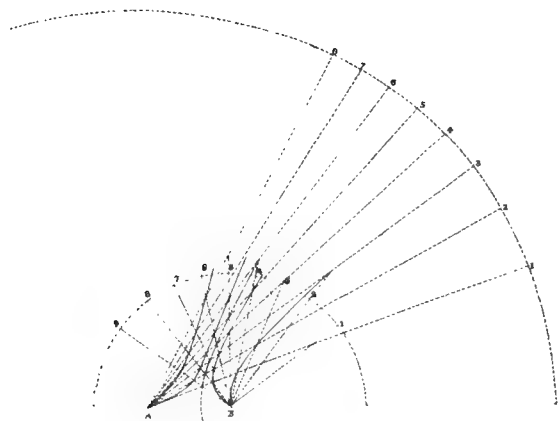


FIG. III.

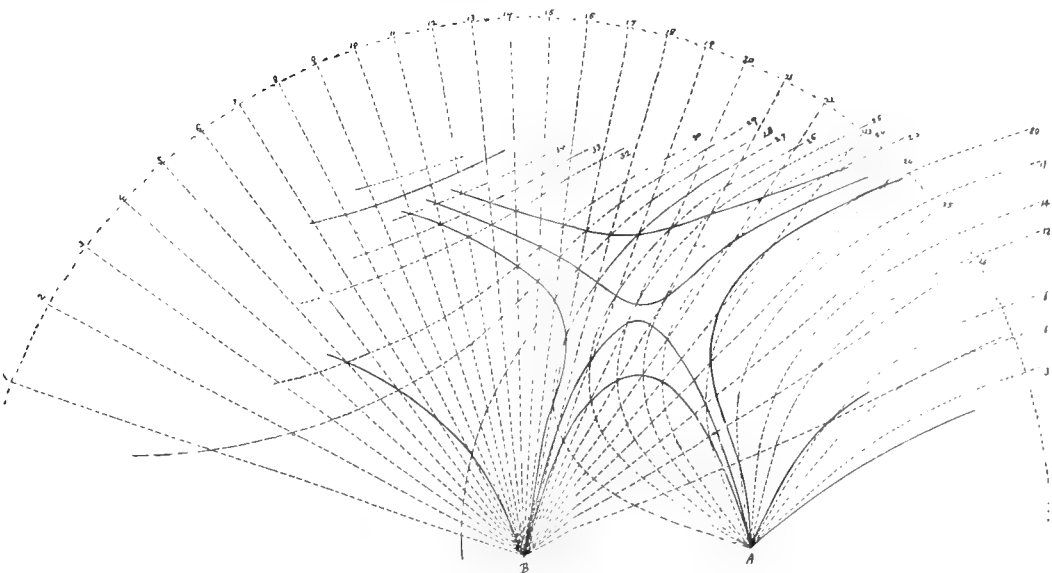


FIG. VI.





INDEX  
THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[SIXTH SERIES.]

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AUGUST 1911.

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XXIV. *On the Calculation of Chladni's Figures for a Square Plate.* By LORD RAYLEIGH, O.M., F.R.S.\*

IN my book on the Theory of Sound, ch. x. (1st ed. 1877, 2nd ed. 1894) I had to speak of the problem of the vibrations of a rectangular plate, whose edges are free, as being one of great difficulty, which had for the most part resisted attack. An exception could be made of the case in which  $\mu$  (the ratio of lateral contraction to longitudinal elongation) might be regarded as evanescent. It was shown that a rectangular plate could then vibrate after the same law as obtains for a simple bar, and by superposition some of the simpler Chladni's figures for a square plate were deduced. For glass and metal the value of  $\mu$  is about  $\frac{1}{4}$ , so that for such plates as are usually experimented on the results could be considered only as rather rough approximations.

I wish to call attention to a remarkable memoir by W. Ritz † in which, somewhat on the above lines, is developed with great skill what may be regarded as a practically complete solution of the problem of Chladni's figures on square plates. It is shown that to within a few per cent. all the proper

\* Communicated by the Author.

† Theorie der Transversalschwingungen einer quadratischen Platte mit freien Rändern, *Annalen des Physik*, Bd. xxviii. S. 737 (1909). The early death of the talented author must be accounted a severe loss to Mathematical Physics.

tones of the plate may be expressed by the formulæ

$$w_{mn} = u_m(x)u_n(y) + u_m(y)u_n(x),$$

$$w'_{mn} = u_m(x)u_n(y) - u_m(y)u_n(x),$$

the functions  $u$  being those proper to a free bar vibrating transversely. The coordinate axes are drawn through the centre parallel to the sides of the square. The first function of the series  $u_0(x)$  is constant; the second  $u_1(x) = x \cdot \text{const.}$ ;  $u_2(x)$  is thus the fundamental vibration in the usual sense, with two nodes, and so on. Ritz rather implies that I had overlooked the necessity of the first two terms in the expression of an arbitrary function. It would have been better to have mentioned them explicitly; but I do not think any reader of my book could have been misled. In § 168 the inclusion of *all*\* particular solutions is postulated, and in § 175 a reference is made to zero values of the frequency.

For the gravest tone of a square plate the coordinate axes are nodal, and Ritz finds as the result of successive approximations

$$\begin{aligned} w &= u_1 v_1 + \cdot 0394 (u_1 v_3 + v_1 u_3) \\ &\quad - \cdot 0040 u_3 v_3 - \cdot 0034 (u_1 v_5 + u_5 v_1) \\ &\quad + \cdot 0011 (u_3 v_5 + u_5 v_3) - \cdot 0019 u_5 v_5 ; \end{aligned}$$

in which  $u$  stands for  $u(x)$  and  $v$  for  $u(y)$ . The leading term  $u_1 v_1$ , or  $xy$ , is the same as that which I had used (§ 228) as a rough approximation on which to found a calculation of pitch.

As has been said, the general method of approximation is very skillfully applied, but I am surprised that Ritz should have regarded the method itself as new. An integral involving an unknown arbitrary function is to be made a minimum. The unknown function can be represented by a series of known functions with arbitrary coefficients—accurately if the series be continued to infinity, and approximately by a few terms. When the number of coefficients, also called generalized coordinates, is finite, they are of course to be determined by ordinary methods so as to make the integral a minimum. It was in this way that I found the correction for the open end of an organ-pipe †, using a series with two terms to express the velocity at the mouth. The calculation

\* Italics in original.

† Phil. Trans. vol. 161 (1870); Scientific Papers, i. p. 57.

was further elaborated in 'Theory of Sound,' vol. ii. Appendix A. I had supposed that this treatise abounded in applications of the method in question, see §§ 88, 89, 90, 91, 182, 209, 210, 265; but perhaps the most explicit formulation of it is in a more recent paper\*, where it takes almost exactly the shape employed by Ritz. From the title it will be seen that I hardly expected the method to be so successful as Ritz made it in the case of higher modes of vibration.

Being upon the subject I will take the opportunity of showing how the gravest mode of a square plate may be treated precisely upon the lines of the paper referred to. The potential energy of bending per unit area has the expression

$$V = \frac{qh^3}{3(1-\mu^2)} \left[ (\nabla^2 w)^2 + 2(1-\mu) \left\{ \left( \frac{d^2 w}{dx dy} \right)^2 - \frac{d^2 w}{dx^2} \frac{d^2 w}{dy^2} \right\} \right], \quad (1)$$

in which  $q$  is Young's modulus, and  $2h$  the thickness of the plate (§ 214). Also for the kinetic energy per unit area we have

$$T = \rho h \dot{w}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$\rho$  being the volume-density. From the symmetries of the case  $w$  must be an odd function of  $x$  and an odd function of  $y$ , and it must also be symmetrical between  $x$  and  $y$ . Thus we may take

$$w = q_1 xy + q_2 xy(x^2 + y^2) + q_3 xy(x^4 + y^4) + q_4 x^3 y^3 + \dots \quad (3)$$

In the actual calculation only the two first terms will be employed.

Expressions (1) and (2) are to be integrated over the square; but it will suffice to include only the first quadrant, so that if we take the side of the square as equal to 2, the limits for  $x$  and  $y$  are 0 and 1. We find

$$\iint (\nabla^2 w)^2 dx dy = 16q_2^2, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\iint \left\{ \left( \frac{d^2 w}{dx dy} \right)^2 - \frac{d^2 w}{dx^2} \frac{d^2 w}{dy^2} \right\} dx dy = q_1^2 + 4q_1 q_2 + \frac{8}{3} q_2^2. \quad (5)$$

\* "On the Calculation of the Frequency of Vibration of a System in its Gravest Mode, with an Example from Hydrodynamics," *Phil. Mag.* vol. xlvii. p. 556 (1899); *Scientific Papers*, iv. p. 407.

Thus, if we set

$$V = \frac{4qh^3}{3(1+\mu)} V', \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we have

$$V' = \frac{1}{2}q_1^2 + 2q_1q_2 + \frac{4}{3}q_2^2 + \frac{4q_2^2}{1-\mu} \quad . \quad . \quad . \quad . \quad (7)$$

In like manner, if

$$T = \frac{2\rho h}{9} T', \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$T' = \frac{1}{2}\dot{q}_1^2 + \frac{6}{5}\dot{q}_1\dot{q}_2 + \dot{q}_2^2\left(\frac{3}{7} + \frac{9}{25}\right) \quad . \quad . \quad . \quad . \quad (9)$$

When we neglect  $q_2$  and suppose that  $q_1$  varies as  $\cos pt$ , these expressions give

$$p^2 = \frac{6qh^2}{\rho(1+\mu)} = \frac{96qh^2}{\rho(1+\mu)a^4}, \quad . \quad . \quad . \quad . \quad (10)$$

if we introduce  $a$  as the length of the side of the square. This is the value found in 'Theory of Sound,' § 228, equivalent to Ritz's first approximation.

In proceeding to a second approximation we may omit the factors already accounted for in (10). Expressions (7), (9) are of the standard form if we take

$$A = 1, \quad B = 2, \quad C = \frac{8}{5} + \frac{8}{1-\mu},$$

$$L = 1, \quad M = \frac{6}{5}, \quad N = \frac{6}{7} + \frac{18}{25};$$

and Lagrange's equations are

$$\left. \begin{aligned} (A-p^2L)q_1 + (B-p^2M)q_2 &= 0, \\ (B-p^2M)q_1 + (C-p^2N)q_2 &= 0, \end{aligned} \right\} \quad . \quad . \quad . \quad (11)$$

while the equation for  $p^2$  is the quadratic

$$p^4(LN - M^2) + p^2(2MB - LC - NA) + AC - B^2 = 0. \quad . \quad (12)$$

For the numerical calculations we will suppose, following Ritz, that  $\mu = .225$ , making  $C = 11.9226$ . Thus

$$\begin{aligned} LN - M^2 &= .13714, & AC - B^2 &= 7.9226, \\ 2MB - LC - NA &= -2 \times 4.3498. \end{aligned}$$

The smaller root of the quadratic as calculated by the usual formula is .9239, in place of the 1 of the first approximation; but the process is not arithmetically advantageous. If we substitute this value in the first term of the quadratic, and

determine  $p^2$  from the resulting simple equation, we get the confirmed and corrected value  $p^2 = .9241$ . Restoring the omitted factors, we have finally as the result of the second approximation

$$p^2 = \frac{96qh^2 \times .9241}{\rho(1+\mu)a^4}, \quad . \quad . \quad . \quad . \quad (13)$$

in which  $\mu = .225$ .

The value thus obtained is not so low, and therefore not so good, as that derived by Ritz from the series of  $u$ -functions. One of the advantages of the latter is that, being *normal* functions for the simple bar, they allow  $T$  to be expressed as a sum of squares of the generalized coordinates  $q_1$  &c. As a consequence,  $p^2$  appears only in the diagonal terms of the system of equations analogous to (11).

From (11) we find further

$$q_2/q_1 = -.0852,$$

so that for the approximate form of  $w$  corresponding to the gravest pitch we may take

$$w = xy - .0852 xy(x^2 + y^2), \quad . \quad . \quad . \quad (14)$$

in which the side of the square is supposed equal to 2.

XXV. *An Experimental Investigation on the Reflexion of Light at certain Metal-Liquid Surfaces.* By LYNDE P. WHEELER, Assistant Professor of Physics, Sheffield Scientific School of Yale University\*.

#### *Introduction.*

WHEN light is incident on a transparent substance at an angle whose tangent has the numerical value of the index of refraction of the material, theory, as embodied in the Fresnel equations, demands that the reflected light should be plane polarized in the plane of incidence. Experience teaches, however, that for but a very few substances, solid or liquid, is this true. Most substances show at this angle an elliptic polarization of small ellipticity. The ellipticity (defined as the ratio of the amplitudes of the components of the vibration parallel and perpendicular to the plane of incidence) is found to be sometimes positive and sometimes negative. (Positive ellipticity corresponds to a counter-clockwise description of the ellipse when viewed from the side of the incident light.)

\* Communicated by the Author.

That this well-nigh universal though small discrepancy between theory and experiment cannot be entirely assigned to contamination of the reflecting surface seems to have been definitely settled by the experiments of Lord Rayleigh on very clean water surfaces\*. He found that as the surface was made progressively cleaner, the negative ellipticity previously observed became numerically smaller, passed through a zero value, and for the cleanest surfaces obtainable assumed a very small positive value. On the other hand, Drude, working with the fresh cleavage surfaces of transparent crystals where the chance of surface contamination is very remote, found that within the limits of error of observation the ellipticity vanished†. It would thus seem to be established that the theory stands in need of correction in the case of reflexion from liquids, while remaining entirely competent in the case of solids.

Now the boundary conditions from which the equations of Fresnel are deduced assume an abrupt, discontinuous change in physical properties as one passes through the surface separating the two media. As such physical discontinuity is, *a priori*, highly improbable, it is natural to seek the source of the observed discrepancies in a thin transition layer where the two media interpenetrate, and the physical properties change continuously, though rapidly, between the constant values they possess beyond the limits of the layer on either side. On this hypothesis it is natural to expect a thinner transition layer, and hence a closer approximation to the conditions of a discontinuous change, in the case of solids than of liquids. Thus, admitting that such layers must exist in all cases, we must conclude from the experiments mentioned, that it is only in the case of liquids that they attain a sufficient thickness to be appreciable.

But while the existence of the transition layer seems a fairly certain inference from the phenomena of reflexion, it is equally certain that the greater part of the divergences of experiment from the predictions of theory are to be ascribed to films of surface contamination due to dirt or polisher. Such films may be exceedingly thin—of the same order of magnitude in fact as the transition layer. In any given case both the layer and the film may be present and the observed ellipticity be due to their combined action. The principal difference in the effect produced by these two causes would be due to the fact that in the case of the transition layer its index of refraction must vary between those of the two

\* Phil. Mag. ser. 5, vol. xxxiii, 1892, p. 1.

† Wied. Ann. xxxvi, 1889, p. 532.

media ; while in the case of the film of surface contamination its index should be approximately constant, and its value might be greater or less than or intermediate between those of the two media.

Mathematically the effects to be expected from either the transition layer or the film can be thrown into identical form, the only difference in the two cases being that imposed on the interpretation of the results by the possible values of the index of refraction, as indicated above. The mathematical theory of such layers or films has been worked out in great detail by Drude\*, who has shown that on the assumption that the thickness of the film is small compared with the wave-length of the light employed, its effect can be expressed as a correction term to the ordinary Fresnel equations. The form of this correction term shows that when the reflexion takes place from the surface of a substance of greater index than that in which the light is incident, we should expect a positive ellipticity at the polarizing angle for any film which has an index lying between those of the two media, and a negative ellipticity for a film with a greater index than that of either medium. Thus a real transition layer can theoretically produce only a positive ellipticity, while a negative ellipticity must always be attributed to films of surface contamination with indices greater than that of the reflecting substance. Of course *all* of an observed positive ellipticity may not be due to a transition layer, for the matter contaminating the surface may have an index intermediate between those of the two media ; but a negative ellipticity is theoretically a certain criterion of a film of contamination. Lord Rayleigh's experiments mentioned above are thus in striking accord with the theory.

The same general considerations hold in the case of the reflexion from metals. Here, however, since metals naturally produce an elliptic (or a circular) polarization at all angles of incidence, the effect of the transition layer or film of contamination will be to change the ellipticity and the phase difference of the two components of the vibration from the values they would have if the film were not present. The theory, based on the same assumption as in the case of the reflexion from transparent substances†, shows that, providing the index of refraction of the film or layer is greater than

\* Wied. *Ann.* xxxvi. 1889, p. 865. A brief development of the theory of the transition layer is given in the 'Theory of Optics,' by Drude, translated by Mann and Millikan, 1902, p. 217. Also in Winkelmann, *Handbuch der Physik*, 2<sup>e</sup> Aufl. 1906, vol. vi. p. 1256, and in the 'Physical Optics,' by Wood, p. 296.

† Wied. *Ann.* xxxvi. 1889, p. 865.

unity, the ellipticity should be slightly increased and the phase difference markedly decreased by the presence of such a film or layer. Expressed in terms of the principal incidence and azimuth instead of the phase difference and ellipticity, the theory predicts that the effect of the film should be to decrease the principal incidence markedly and to increase the principal azimuth but a very little. Unlike the result for the reflexion from transparent substances, the sign of the effect is independent of the magnitude of the index of refraction of the reflecting medium, unless that should be less than unity.

We have here, then, no such criterion as before to enable us to distinguish between films of surface contamination and a real transition layer. A possible exception to this statement is the case of those metals which have an index of refraction less than unity. That some metals, notably gold, silver, and copper, do possess such small values of the index seems certain, since the same result is yielded by the reflexion and the direct transmission methods. With these substances it might be expected that the transition layer would have an index less than unity, and that consequently, according to the theory, the phase difference would be increased and the ellipticity decreased over the values they would have if no such layer were present. However, from general considerations as to the degree to which it would be possible for the two media to interpenetrate and produce a transition layer, it would seem unlikely that we could obtain any evidence as to its existence; exactly as any such evidence fails in the case of reflexion from transparent solids. And in confirmation of this expectation it is found that for all metals, increasing the cleanliness of the surface shows uniformly an increase of the phase difference and a decrease of the ellipticity; there is never any indication of any reversal of the sign of the effect. So that it is fair to assume that when perfect cleanliness has been attained, the correct values of the phase difference and the ellipticity are yielded by experiment; the effect of the transition layer being negligible.

Further light on the question of the transition layer is afforded by experiments on the reflexion from metal mirrors immersed in transparent liquids. Here the uncorrected theory leads to an expression for the index of refraction of the liquid ( $n'$ ) in terms of the observed phase differences and ellipticities in air and in the liquid respectively\*. An examination of the recorded observations of this nature shows, however, very considerable discrepancies between the values

\* See below, under heading "Theory."



so calculated and those given by the direct refraction methods ( $n_0$ ). In the following Table are given the values of  $n'$  and  $n_0$ , as calculated from the experimental results. It includes all the observations on record\*.

	$n'$ .	$n_0$ .	Observer.
Gold in Water .....	1.30	1.33	Conroy.
" CS <sub>2</sub> .....	1.54	1.64	"
Silver in Water .....	1.25	1.34	Quinke.
" " .....	1.25	1.33	Conroy.
" " .....	1.43	1.34	Sissingh.
" Turpentine .....	1.44	1.47	Quinke.
" CCl <sub>4</sub> .....	1.35	1.46	Conroy.
Copper in Water .....	1.33	1.33	Drude.
" Alcohol .....	1.32	1.37	"
" Cassia Oil .....	1.50	1.61	"
" CS <sub>2</sub> .....	1.52	1.63	"
Mercury in Water .....	1.24	1.33	Des Coudres.
" Alcohol .....	1.28	1.36	"
" HCl (dilute) .....	1.44	1.39	"
" " (conc.) .....	1.30	1.39	"
" Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (conc.) .....	1.32	1.42	"
" " (sup. sat.) ...	1.28	1.43	"
" Petroleum .....	1.38	1.44	"
" Chloroform .....	1.37	1.44	"
" Olive Oil .....	1.47	1.47	"
" Turpentine .....	1.25	1.47	"
" " .....	1.32	1.47	"
" CS <sub>2</sub> .....	1.59	1.63	"
" " .....	1.48	1.63	"

Now it is impossible to ascribe these discrepancies in every case to films of surface contamination; for they occur for those metals (notably copper and mercury) for which entirely satisfactory results in air have been obtained, and under circumstances apparently precluding the formation of any chemical film. Hence, as we have seen that it is highly probable that a perfectly clean metal possesses no appreciable transition layer when in contact with air, it is only possible to ascribe these discrepancies to a transition layer due to the liquid. Now, an inspection of the above Table shows that the index calculated from the reflexion from the metal is in all but four cases less than that deduced by the direct refraction methods. On the theory as developed

\* The values are taken from a paper by Drude, Wied. *Ann.* xxxix. 1891, p. 539. The calculations have been verified, except in the case of the experiments of Sissingh and Des Coudres, to whose original papers I have not had access.

by Drude \*, this result must be interpreted as due to a film or layer having an index less than that of the liquid. This suggests that the effect is due to a film of air or other gas caught between the liquid and the mirror, since the transition layer of a liquid-air surface would have an index less than that of the liquid. It is, moreover, natural to expect the presence of such films due either to entrainment in the act of immersion or to dissolved gas in the liquid, more probably the former.

On the other hand, if it is assumed that no such gaseous film is present, the observed discrepancies must be attributed to a transition layer due to the liquid. In view of the fact that the effects of the transition layer in the case of transparent solids in air are inappreciable, it would seem that the layer in question here cannot be a region of interpenetration of the metal and the liquid. Consequently we must conclude (if we reject the possibility of the gaseous film) that the observed discrepancies are due to a layer at the surface of the liquid which is independent of the medium with which it may be in contact and which has optical properties different from those in the interior. According to the theory, the index of such a layer will be less than that of the interior if  $n'$  is less than  $n_0$ ; while its index should be greater when  $n'$  is greater than  $n_0$ . Such effects might possibly be expected as a result of surface tension.

There are thus two possible explanations of the observed discrepancies. It would seem worth while, therefore, to eliminate the possibility of gaseous films between the mirror and the liquid. The desirability of doing this has been pointed out by Drude †, but so far as I can ascertain, it has not, up to the present time, been attempted. Drude has expressed the opinion that there would still remain evidence of a transition layer when such gaseous films have been removed ‡. But this opinion is supported by no evidence which cannot be interpreted, as we have seen, in another manner. Hence I have attempted in the investigation reported in this paper to see if any residual effect of a transition layer remains, when the possibility of the presence of a gaseous film between the mirror and the liquid is reduced to a minimum.

\* Wied. *Ann.* xxxix. 1891, p. 539. See also below, under heading "Theory."

† Wied. *Ann.* xxxix. 1891, p. 545. Also Winkelmann, *Handbuch der Physik*, 2<sup>nd</sup> Aufl. 1906, vol. vi. p. 1308.

‡ Winkelmann, *loc. cit.*

Theory.

The theory of metallic reflexion in transparent liquids is not developed in any of the ordinary works of reference, though it is of course accessible in the original memoirs. So it may not be out of place to give a brief resumé of the theory here. We start with the equation

$$\frac{1 + \tan \psi e^{i\Delta}}{1 - \tan \psi e^{i\Delta}} = \frac{\sin \phi \sin \chi}{\cos \phi \cos \chi}, \quad \dots \quad (1)^*$$

where  $\psi$  is the azimuth of the restored polarization (the angle whose tangent gives the ratio of the amplitudes of the two components of the reflected vibration when the incident vibration is polarized in a plane making an angle of  $45^\circ$  with the plane of incidence;  $\tan \psi$  is what we have called the "ellipticity" in the introduction),  $e$  is the Napierian base,  $i = \sqrt{-1}$ ,  $\phi$  and  $\chi$  are the angles of incidence and refraction respectively; while  $\Delta$  is the phase difference between the two components of the reflected vibration.

In the case of the reflexion in a vacuum (or air) we have the relation

$$\frac{\sin \phi}{\sin \chi} = \sqrt{K}, \quad \dots \quad (2)$$

where  $K$  is the dielectric constant of the reflecting medium. In the case of a metal this must be supposed complex and the real part of  $\sqrt{K}$  is the index of refraction. If we substitute for  $\chi$  in (1) from (2), replace the exponential by its equivalent trigonometrical expression, and rationalize the denominator of the left-hand side of (1), we obtain

$$\frac{\cos 2\psi(1 + i \sin \Delta \tan 2\psi)}{1 - \cos \Delta \sin 2\psi} = \frac{\sin \phi \tan \phi}{\sqrt{K} - \sin^2 \phi}.$$

This may be simplified by making the following substitutions :

$$\left. \begin{aligned} \sin \Delta \tan 2\psi &= \tan Q; \quad \cos \Delta \sin 2\psi = \cos P; \\ \cos 2\psi &= \cos Q \sin P; \quad S = \tan \frac{P}{2} \sin \phi \tan \phi; \end{aligned} \right\} \quad \dots \quad (3)$$

which yield

$$e^{iQ} = \frac{S}{\sqrt{K} - \sin^2 \phi}. \quad \dots \quad (4)$$

\* The derivation of this equation may be found in any standard text on Optics; *e. g.*, those of Drude, Schuster; Wood.

In the case of the reflexion in a transparent medium of index of refraction  $n_0$ , we have in place of (2) the relation

$$n_0 \frac{\sin \phi}{\sin \chi} = \sqrt{K}.$$

Substituting from this in (1) and performing the same operations and making the same substitutions as before, we get

$$e^{iQ_0} = \frac{n_0 S_0}{\sqrt{K - n_0^2 \phi}}. \quad \dots \dots \dots (5)$$

Dividing (4) by (5) and substituting for the radical in the denominator its value from (4) we get

$$n_0 \frac{S_0}{S} e^{i(Q - Q_0)} = \frac{e^{iQ}}{S} \sqrt{K - n_0^2 \sin^2 \phi}.$$

Using in this the value of  $K$  from (4),

$$K = \frac{S^2}{e^{i2Q}} + \sin^2 \phi,$$

we obtain

$$n_0 \frac{S_0}{S} e^{i(Q - Q_0)} = \sqrt{1 - \frac{\sin^2 \phi}{S^2} (n_0^2 - 1) e^{i2Q}}.$$

Expanding the radical and retaining no terms higher than the second in  $\frac{\sin \phi}{S}$ \*, and substituting

$$\delta = -\frac{1}{2} \frac{\sin^2 \phi}{S^2} (n_0^2 - 1) \cos 2Q; \quad \dots \dots (6)$$

$$\epsilon = \frac{1}{2} \frac{\sin^2 \phi}{S^2} (n_0^2 - 1) \sin 2Q; \quad \dots \dots (7)$$

we have, on equating the real and imaginary parts of each side, approximately\*,

$$n_0 = \frac{S}{S_0} (1 + \delta); \quad \dots \dots \dots (8)$$

$$Q - Q_0 = -\epsilon. \quad \dots \dots \dots (9)$$

Thus from the observed values of  $\Delta$  and  $2\psi$  we can calculate, by means of equations (3) and (6), the right-hand side of equation (8). Calling the value so calculated  $n'$ , we

\* These approximations are justified by the magnitudes of  $S$  and  $Q$  as found from experiment.

have the result  $n_0 = n'$ ; or, the index of refraction of the liquid calculated by refraction methods should be the same as that deduced from the change of phase and the ellipticity produced by the metal.

If there are transition layers or films of surface contamination present, their effect may be expressed as a correction term to equation (5) as follows:

$$e^{iQ_0} = \frac{n_0 S_0}{\sqrt{K - n_0^2 \sin^2 \phi}} (1 - i \sqrt{KA}) \dots (10)^*$$

If we assume that there is but the one transition layer, that between the liquid and the gas film, the value of A will be

$$A = \frac{2\pi}{\lambda} \int_0^L \left( \frac{n_0^2}{n_1^2} - 1 \right) dl \dots (11)^*$$

where  $\lambda$  is the wave-length of the light employed, L the thickness, and  $n_1$  the index of the layer. Of course a similar correction term to equation (4) can be written down, but under the assumption that a metal in air possesses no appreciable transition layer, that may be omitted.

Proceeding now as before, we obtain the equation

$$n_0 \frac{S_0}{S} e^{i(Q-Q_0)} = \sqrt{1 - \frac{\sin^2 \phi}{S^2} (n_0^2 - 1)} e^{i2Q} (1 + i \sqrt{KA}).$$

Substituting in the correction term the approximate value of  $\sqrt{K}$  from (4),

$$\sqrt{K} = \frac{S}{e^{iQ}},$$

we have, on expanding and making the substitutions (6) and (7),

$$n_0 = \frac{S}{S_0} (1 + \delta + AS \sin Q); \dots (12)$$

$$Q - Q_0 = -\epsilon + AS \cos Q \dots (13)$$

If we set as before,  $n' = S/S_0 (1 + \delta)$ , equation (12) can be written

$$n' = n_0 (1 - AS \sin Q), \dots (14)$$

since both  $\delta$  and  $AS \sin Q$  are small quantities.

\* Since the results of the experiments I have to report in this paper seem to show that  $A=0$  for the liquids used, it seems scarcely worth while in this place to devote the very considerable amount of space which would be required, to the derivation of equations (10) and (11). The derivation is given in full in the papers of Drude in *Wied. Ann.* already cited.

By means of this equation and equation (11), we can compare the results of experiment with theory. Thus from the latter we see that if  $n_1$  is less than  $n_0$ , then  $A$  will be positive and consequently by equation (14)  $n'$  should be less than  $n_0$ . This, then, is the result we should expect in case there is a gaseous film between the mirror and the liquid; or, providing that is eliminated, it is the result to be expected in the event that a real transition layer (belonging to the liquid alone, as we have seen), exists. Similarly, if  $n_1$  is greater than  $n_0$ , we see from equation (11) that  $A$  will be negative, and consequently from equation (14) that  $n'$  should be greater than  $n_0$ . Such a result would mean a film of greater index than that of the liquid, and hence must be attributed either to films of surface contamination or to a real transition layer, no gaseous film being possible under these conditions. Finally, we see that if  $A=0$ ,  $n'=n_c$ , and this is the result to be expected if no films of any kind are present.

Thus if we can make sure that there is no gaseous film nor any film of surface contamination present, a value of  $n'$  less than  $n_0$  would indicate that at its surface the liquid has an index of refraction less than in the interior; while a value of  $n'$  greater than  $n_0$  would be evidence that the index of the liquid at the surface is greater than in the interior.

#### *Experimental Arrangements.*

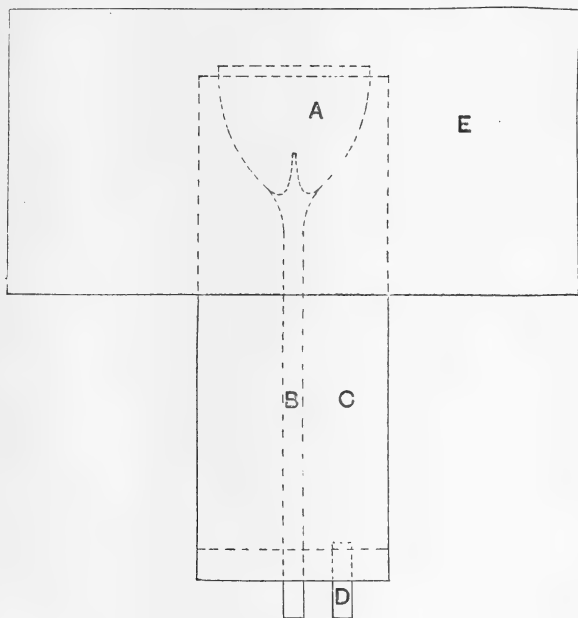
In repeating these experiments which have been performed so many times and by such competent observers, it was sought to improve upon their results in two directions: first in securing a mirror which should be more free from surface contamination than those used before, and second in reducing the possibility of a gaseous film between the mirror and the liquid to a minimum. On account of the difficulties in the way of certainly getting rid of films of surface contamination in solid mirrors, it was decided to attempt to attain the first object by using a mercury mirror. The advantages of such a mirror are, first, that it admits of obtaining an extraordinarily clean surface much more easily than any other metal; second, exactly similar surfaces can be easily and quickly reproduced; and third, the degree of cleanliness attained can be estimated better than with mirrors of solid metal. The method of cleaning the surface by stretching the dirt to the edges (first suggested, in the case of water, by Lord Rayleigh\*) was adopted in the form recommended by Röntgen†. This is described below.

\* Phil. Mag. [5] xxx. 1890, p. 392.

† Wied. Ann. xlv. 1892, p. 152.

It was feared at first that the attainment of the second object would present formidable if not insuperable difficulties. Drude has suggested the possibility of removing the film of gas by heating\*, but this would involve obvious complications and difficulties. As mentioned in the introduction, it seems probable to expect that the gas film is introduced by entrainment in the act of immersion. Hence it was decided to produce the clean mercury surface *while* the mirror was immersed. The method of Röntgen for producing the clean surface lends itself very readily to this purpose; and it would seem from the results obtained that complete success in this important object has been attained. The form which the apparatus for producing the mirrors finally took is shown in the figure.

A glass tube of about 4 cm. diameter was drawn down to form a funnel-shaped vessel (A), into the neck of which was



sealed a small tube (B) having its end drawn out to a capillary point and projecting into the funnel. This tube, passing through a cork at the bottom of the cylindrical iron vessel (C) which surrounded the funnel, was supported so that the mouth of the funnel (ground to a plane) came slightly above the top of the cylinder. Another tube (D)

\* Wied. Ann. xxxix. 1891, p. 545.

through the cork (which was provided with a suitable stop-cock, not shown in the figure) carried away the mercury which overflowed the funnel. The iron cylinder passed through the bottom of an open rectangular iron box (E) and projected to within about 1.5 cm. of its top. This box served to hold the liquids under which the reflexion was observed.

This surface cleaning apparatus was mounted on a stand furnished with levelling screws to enable one to adjust the mouth of the funnel accurately to a horizontal plane. The stand was also provided with a rack and pinion to give the vertical adjustment necessary to bring the reflecting surface to the centre of the spectrometer table. A reservoir of mercury hung at a higher level than that of the funnel was connected with the tube (B) by a flexible tube provided with a suitable pinchcock. In order to secure a mirror sufficiently free from vibration, it was found necessary to mount the stand in a Julius suspension.

The operation of producing a clean surface was simply to allow the mercury to overflow the edge of the funnel rapidly for a few seconds. If care is taken to make the overflow uniform all around the edge (accomplished by adjusting the levelling-screws), surfaces of extreme cleanliness can easily be obtained. The test of the cleanliness is the behaviour of a drop of water placed on the surface. In making the test it is essential that the drop itself be clean. This is most easily done in practice by dipping a piece of platinum wire (cleaned by heating) beneath the surface of a beaker of distilled water, and removing the adhering drop quickly to the mercury surface. If the surface is really clean, the drop is immediately stretched out to the edge in a film of invisible thickness. The appearance of a mercury surface to the eye is no test at all of its cleanliness; it may seem to be a perfect mirror and yet the drop remain in a hemispherical form when placed on it, unless it has been recently cleaned in the manner described. It is not necessary to start with especially clean mercury—it cleans itself in a very short time. Nor is it necessary to test the cleanliness of the surface except after each fresh filling of the reservoir. A good surface gets contaminated in the air in a brief time, but retains its cleanliness long enough to permit the necessary observations to be taken comfortably; while a fresh surface can be obtained easily and quickly.

Thus it is reasonably certain that the reflecting surfaces used were free from surface contamination. Of course it is not so certain, *a priori*, that the film of gas was removed when the mirror was submerged. It is natural to expect,



however, that the rapid overflowing of the mercury would tend to carry away any such film and leave a more perfect contact between the two media. And from the final result of these experiments it would seem that this expectation is fully justified. During the course of a set of observations under a liquid it was of course necessary to close the overflow tube (D); consequently the cylinder (C) was made large enough to hold all of the mercury which it was necessary to allow to overflow in the course of such a set. The liquid thus displaced from the box (E) was made to overflow at one corner and was caught in a suitable vessel.

In order to avoid any deviation of the beam of light by refraction at the free surface of the liquid, glass tubes terminated by plane parallel glass ends were carried in suitable brass holders by both the collimator and telescope arms; when the mirror was in position, the ends of these tubes were just submerged in the liquid in (E). The length of the box (E) was made as great as the space between the tube-holders would allow, in order to obtain as large an angle of incidence as possible. The space thus available was, however, too small to permit the use of angles of incidence greater than  $60^\circ$ , which, though lessening the precision attainable in this kind of experiment, still yielded ample accuracy for the ends in view.

The apparatus for measuring the phase-difference and azimuth of restored polarization was of a familiar type and needs but brief description. The spectrometer\* was one by the Société G  n  voise, arranged so that the table could be swung to a vertical position to accommodate a horizontal mirror. The collimator arm carried the polarizing nicol behind the lens; the Babinet compensator was mounted before the objective of the telescope; while the analysing nicol was carried at the other end of the telescope tube. The nicols and compensator came with the spectrometer and were of good quality. By means of a second lens which could be inserted behind the analyser, and an extra draw-tube, the eyepiece could be focussed on the compensator fringes. Since these are not definite objects on which to focus, a small circular diaphragm was inserted behind the last lens of the ocular in order to avoid a small residual parallax which was otherwise necessarily present. These modifications of the apparatus as originally received from the Soci  t   G  n  voise and also the holders for the glass tubes and the surface-cleaning apparatus described above,

\* This was obtained by the aid of a grant from the Bache fund of the National Academy of Science.

were made in the instrument shop of the Sheffield Scientific School. The divided circle of the spectrometer table could be read to 20'' and those of the nicols to 6' of arc. The source of light used was that obtained from the sodium flame of a small blast-lamp fed with oxygen.

#### *Measurements.*

The preliminary adjustments of the apparatus, *i. e.* making the axes of collimator and telescope to intersect the axis of the spectrometer table orthogonally, and the adjustment of the axes of the nicols to parallelism with those of the collimator and telescope, were made in the usual manner. The positions of the polarizer giving light polarized in the plane of incidence was determined by reflexion from water at the polarizing angle. The water surface was cleaned in the same manner as described above for the mercury. This plane was determined several times in the course of the investigation and with several minor modifications of method. Thus, sometimes the extinction position of the analyser was determined with the reflexion taking place at the polarizing angle, and then that of the polarizer by getting its "crossed" position with reference to the analyser when the two were put in line; or, sometimes the extinction position of the polarizer for the reflexion at the polarizing angle was determined directly, the beam of light being sent through the apparatus in the reverse direction; another modification was the use of glass of known index in place of water. None of these various determinations yielded a position of the polarizer differing from that of any other determination by an amount as large as the probable error of the readings. The result of all these determinations gives a value of  $156^{\circ}58$  for the position of the polarizer. The probable error is less than  $0^{\circ}003$ .

The calibration of the compensator was made with the polarizer in all four of the positions yielding light vibrating in a plane making an angle of  $45^{\circ}$  with the plane of incidence. For each position the reading for the centre fringe and the first fringe on either side of the centre was determined as the mean of fifteen settings. Thus each position of the polarizer yields two values of the displacement of the compensator corresponding to a change of phase of  $360^{\circ}$ . The results, in terms of turns of the compensator screw, follow:—

Polarizer set to .....	20°58	201°58	111°58	290°58	
Compensator (left) ...	8.988	8.967	8.982	8.962	
„ (right) ...	8.971	8.982	8.974	8.979	
„ (av.) .....	8.980	8.975	8.978	8.970	<u>8.9756 ± 0.0021</u>

Compensator left or right means that the first fringe to the left or right of the central one was under the cross-wires. On two occasions in the course of the investigation it became necessary to take the compensator to pieces, once to clean it and the second time to replace the cross-wires. On each occasion it was re-calibrated, and both times with the same result within the probable error of the determinations. The constant of the compensator, *i. e.* the factor by which its readings must be multiplied in order to reduce them to degrees, deduced from the above readings is 40.11. The position of the central fringe (zero point of the compensator) was found to vary slightly with temperature, but otherwise was constant. The maximum variation observed was 0.035 turns. The scale on the compensator is so placed that its direct readings yield the supplement of the angle of phase-difference rather than the angle itself.

The observations of the phase difference and the angle of restored polarization were made in the following manner in every case:—(1) With both the telescope and collimator arms level and the surface-cleaning apparatus lowered out of the way, the zero point of the compensator was determined as the mean of at least twelve settings taken coming up from both directions. (2) With the two arms set to give an angle of incidence  $\phi = 60^\circ$ , the mirror was brought into position, adjusted and cleaned in the manner which has been described. (3) With the polarizer set to give light vibrating in a plane inclined at an angle of  $45^\circ$  to the plane of incidence, the displaced position of the central fringe was observed (again as the mean of at least twelve settings from each direction), and the position of the analyser making the fringes blackest was determined. For this last at least twenty-four settings were made in each case. (4) With the polarizer set to give light vibrating in the other  $45^\circ$  plane, the compensator and analyser positions were again determined and with the same number of readings for each. (5) Finally, with the arms brought back into line, the zero point was again determined as in (1), so as to be able to take account of any temperature change in the compensator. The reflecting surface was renewed, of course, as often as might be necessary in the course of a set of observations.

The phase difference is obtained from the difference of the compensator readings of (3) and (4) and those of (1) and (5). The double angle of restored polarization is the difference of the positions of the analyser in (3) and (4).

There were made in all nine complete sets for  $\Delta$  and  $2\psi$  as described above: four in air, three in water, and one each

244 *Reflexion of Light at certain Metal-Liquid Surfaces.*

in the HCl and turpentine. The results are shown in the following table. In the first column are given the observed values of the displacement of the centre fringe in terms of turns of the compensator screw, and in the second the directly observed values of  $2\psi$  (or  $2\psi_0$ ).

	Comp.	$2\psi$ or $2\psi_0$ .
Air .....	$0.7538 \pm 0.0041$	$81^\circ.04 \pm 0^\circ.35$
" .....	$0.7549 \pm 0.0018$	$81^\circ.54 \pm 0^\circ.19$
" .....	$0.7550 \pm 0.0017$	$81^\circ.32 \pm 0^\circ.54$
" .....	$0.7548 \pm 0.0052$	$81^\circ.46 \pm 0^\circ.23$
" (av.) .....	$0.7546 \pm 0.0017$	$81^\circ.34 \pm 0^\circ.18$
Water .....	$0.9975 \pm 0.0035$	$81^\circ.65 \pm 0^\circ.48$
" .....	$0.9935 \pm 0.0010$	$82^\circ.05 \pm 0^\circ.35$
" .....	$0.9934 \pm 0.0039$	$81^\circ.74 \pm 0^\circ.20$
" (av.) .....	$0.9948 \pm 0.0020$	$81^\circ.81 \pm 0^\circ.16$
HCl .....	$1.0030 \pm 0.0099$	$81^\circ.91 \pm 0^\circ.35$
Turpentine .....	$1.0935 \pm 0.0069$	$82^\circ.08 \pm 0^\circ.34$

From the average values above, the values of  $\pi - \Delta$  (or  $\pi - \Delta_0$ ) are computed by multiplication with the compensator constant; while the values of  $Q$  (or  $Q_0$ ),  $P$  (or  $P_0$ ),  $S$  (or  $S_0$ ),  $\delta$  and  $n'$  are calculated by equations (3), (6), and (8). The results of the computations are given in the next table.

	$\Delta$ or $\Delta_0$ .	$Q$ or $Q_0$ .	$P$ or $P_0$ .	$S$ or $S_0$ .	$\delta$ .	$n'$ .
Air .....	$149^\circ.73 \pm 0^\circ.07$	$73^\circ.19$	$148^\circ.63$	$5.343$		
Water .....	$140^\circ.10 \pm 0^\circ.08$	$77^\circ.36$	$139^\circ.40$	$4.055$	$0.0084$	$1.329 \pm 0.005$
HCl .....	$139^\circ.73 \pm 0^\circ.40$	$77^\circ.58$	$139^\circ.10$	$4.024$	$0.0086$	$1.340 \pm 0.015$
Turpentine. ....	$136^\circ.35 \pm 0^\circ.28$	$78^\circ.61$	$135^\circ.78$	$3.693$	$0.0127$	$1.465 \pm 0.011$

Finally, samples of liquids used were put in a hollow prism and their indices determined in the usual way from the angle of the prism and the angle of minimum deviation. The values thus obtained for  $n_0$  were

	$n_0$ .
Water .....	$1.3320$
HCl .....	$1.3375$
Turpentine .....	$1.4690$

These values are certainly correct to the third place.

### *Discussion of the Results.*

An inspection of the tables just given shows that in the case of each of the liquids examined,  $n' = n_0$  within the limits of the error of the observations. In view of what has been said in the introduction and in the discussion of the theory

of the experiments, this result indicates that there was present no appreciable film or layer of any description; and consequently, for these liquids at least, the transition layer which has been inferred from the phenomena of the reflexion in air is not independent of the medium with which it is in contact. In other words, the transition layer is to be regarded as a true region of interpenetration of two media; and the fact that it is appreciable in liquids and not in solids must be attributed to the greater freedom of molecular motions in the case of the former, and not to any change in physical properties at the surface brought about by the force of surface tension.

The liquids chosen for this investigation include those for which the previous observations have yielded values of  $n'$  less than  $n_0$ , and one for which a value of  $n'$  greater than  $n_0$  has been found. As the result of this work goes to show that both of these sorts of discrepancy vanish when all possible extraneous films are removed, it would seem a fair inference that all of the discrepancies which have been found previously are to be attributed to the same causes, and that the conclusion deduced from these experiments is a general one.

Sheffield Scientific School of Yale  
University, New Haven, Conn.,  
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XXVI. *On the Number of Electrons concerned in Metallic Conduction.* By J. W. NICHOLSON, M.A., D.Sc.\*

THE electron theory of the conduction of electricity through metals, first developed by Drude, has in the hands of later investigators, and notably of Riecke, Schuster, J. J. Thomson, Lorentz, and Jeans, been placed on a firm footing. But no certainty exists as to the number of free electrons which must be supposed to be present in the atoms of the various metals at ordinary temperatures, in order to account for their optical properties, and in fact no detailed investigation of the matter appears to have been made. It is known that with certain hypotheses the mathematical results are in fair agreement with experiment, but no agreement of so exact a character as can be found in certain results of the kinetic theory of gases, has been obtained. In this paper a preliminary attempt is made to discriminate between certain hypotheses with the aid of experimental results, and it is shown that one hypothesis can be definitely selected as giving

\* Communicated by the Author.

an agreement which is satisfactory within the limits of experimental error, when its results are compared with the experiments hitherto made. Certain conclusions can be drawn as to the exact number of free electrons pertaining to an atom of a metal. This special portion of the paper is speculative, and of a strictly tentative character, but it may be stated at once that the results therein suggested are supported in detail by other experiments which have been made by Drude, and which are not treated in the present paper, but which are to form the subject of a later communication.

The simplest investigation of the number of effective free electrons, proceeding from a minimum of assumptions, was made by Schuster\*, whose conclusion was that the number of free electrons in a metal at ordinary temperatures is equal to the number of atoms, or exceeds that number not more than three times. The formula on which this conclusion was based is equivalent to that of Drude, and makes use of a mean velocity of all the electrons in the element of volume. Jeans† obtained the same formula in another manner.

The general agreement of Drude's theory with the experimental details of the electrical and thermal properties of metals was to some extent negatived by a later investigation of Lorentz‡, in which the velocities of the electrons were treated as subject to Maxwell's exponential law, as in the kinetic theory of gases. The most recent investigation of the matter is that of Prof. H. A. Wilson§, whose mode of treatment is very direct. Wilson also uses the Maxwellian law of velocity distribution, but his formula for the conductivity of the metal under a steady electric force differs from that of Lorentz by a factor  $2/3$ . He also works out the case of frequencies of the applied electric force which can fall within the visible spectrum, neglecting, as in the previous theories to which we have referred, the sympathetic vibrations which may be set up within the molecules of the metal.

It seems to the writer that Wilson's treatment is the most satisfactory yet published, for the problem in which sympathetic vibrations are not set up, and that, from a theoretical point of view, it is complete. The results of the investigation are left in the form of integrals, which, as he states, may be evaluated by graphical methods. But it will appear that such methods are not necessary, for the integrals may be quickly reduced to others of known type, for which exhaustive tables have been constructed. Moreover, the values

\* Phil. Mag. February 1904.

† Phil. Mag. June 1902; July 1909.

‡ *Vide* 'Theory of Electrons.'

§ Phil. Mag. November 1910.

of the quantities concerned are such, in nearly all cases, as to reduce the integrals to first terms in their series representations.

The results thus obtained represent, in the opinion of the writer, the only possible consequences of a rigorous treatment of the problem, and are in a form which admits of ready comparison with the results of other theories. This comparison is the object of the latter part of this paper, in which it is shown, moreover, that these formulæ alone give a good representation of the experimental phenomena. The paper does not propose to deal with the values of other magnitudes, such as the mean free path of the electrons within the solid, or the emissivity of a plate, its scope being strictly limited to an examination of the number of electrons which are effective in conveying the current. This will account for the absence of certain important references, which bear upon this special problem in a more indirect way.

Wilson's mode of treatment of the problem of conduction is essentially that of Jeans, with the added hypothesis that collisions do not sensibly alter the velocities of the electrons. Collisions with atoms do not, because of the much greater mass of an atom, and collisions with atoms are the more numerous. Thus if  $N$  is the number of electrons in a unit of volume, and  $dN$  the number with a *resultant* velocity between  $V$  and  $V+dV$ , then the group  $dN$  has, in a sense, a permanent existence, and can take the place of a "class" of the ions in Drude's theory, although individuals may be entering or leaving the group at any time. If  $u$  is the mean velocity in the group, along the direction  $x$  of the electric force  $X$ , the equation of motion of the group becomes

$$d/dt(mu dN) = Xe dN - umVdN/l_m, \quad . \quad . \quad (1)$$

as derived from a consideration of momentum gained and lost by the group. The mass of the electron, of whatever nature, is  $m$ , a magnitude to be regarded as effectively constant. The charge on any electron is  $e$ , and  $l_m$  denotes  $(\pi n R^2)^{-1}$ ,  $n$  being the number of atoms in the unit of volume, and  $R$  the sum of radii of electron and atom.

For motion under a periodic force  $X = a \cos pt$ , of frequency  $p/2\pi$ , the solution of this equation is

$$u dN = ea dN \cos (pt - \delta) / m(p^2 + V^2/l_m^2)^{\frac{1}{2}}, \quad . \quad . \quad (2)$$

where  $\tan \delta = pl_m/V$ .

The mean velocity along  $x$  of the electrons in the whole volume is  $u_0$ , where

$$Nu_0 = \int u dN, \quad . \quad . \quad . \quad (3)$$

where the integration extends over all the groups. If the

law of distribution of velocity is that of Maxwell, so that  $dN$ , the number of electrons whose velocity is between  $V$ ,  $V + dV$ , satisfies

$$dN = 4\pi N (q/\pi)^{\frac{3}{2}} V^2 e^{-qV^2} dV, \quad . \quad . \quad . \quad (4)$$

where  $q$  is determined in the usual way in terms of the mean velocity of agitation, then

$$u_0 = \frac{4\pi ea}{m} \left(\frac{q}{\pi}\right)^{\frac{3}{2}} \int_0^\infty \frac{\cos(pt - \delta) e^{-qV^2} V^2 dV}{(p^2 + V^2/l_m^2)^{\frac{3}{2}}}. \quad . \quad . \quad (5)$$

If  $\sigma$  is the conductivity,  $\frac{1}{2}a^2\sigma$  is the mean rate of production of heat in the unit of volume on account of the electric flow. This rate is also the mean value of  $Ne u_0 a \cos pt$ , from which may be deduced

$$\sigma = 2q\sigma_0 \int_0^\infty \frac{V e^{-qV^2} dV}{1 + \pi p^2 m^2 \sigma_0^2 / 4q V^2 N^2 e^4}, \quad . \quad . \quad (6)$$

where  $\sigma_0$  is the steady conductivity. These are the important results in the part of Wilson's paper with which we are concerned. It is stated that this formula gives, by graphical methods, values of  $N$  in most cases about twice as large as those derived from the formula of Schuster and Jeans,

$$\sigma/\sigma_0 = (1 + p^2 m^2 \sigma_0^2 / N^2 e^4)^{-1}, \quad . \quad . \quad . \quad (7)$$

valid when all the electrons have the same velocity of agitation.

On the basis of the equation of motion of a group, which is the essential feature of Wilson's investigation, differing in its last term from that of Jeans, let us consider the optical constants of a metal more minutely, on the simple lines developed by Schuster. With an electric force  $ae^{-ipt}$ , for which a real value may be inserted at the end, the equation of motion of the group is

$$md/dt (u dN) + mV (u dN)/l_m = ea dN e^{-ipt}, \quad . \quad . \quad (8)$$

whose solution is

$$u dN = -\frac{ea}{m} dN (ip - V/l_m)^{-1} e^{-ipt},$$

or

$$u dN = \frac{ea dN (ip + V/l_m)}{p^2 + V^2/l_m^2} e^{-ipt}, \quad . \quad . \quad (9)$$

and applying Maxwell's law, the mean velocity along the direction of the force is

$$u_0 = \frac{4\pi ea}{m} \left(\frac{q}{\pi}\right)^{\frac{3}{2}} e^{-ipt} \int_0^\infty \frac{V^2 dV (ip + V/l_m) e^{-qV^2}}{p^2 + V^2/l_m^2} \quad . \quad . \quad (10)$$



The current is  $Neu_0 = i_1$ ,

$$\text{or } i_1 = a (A + ipB) e^{-ipt}, \quad . . . . (11)$$

where

$$(A, B) = 4\pi N \frac{e^2}{m} \left(\frac{\gamma}{\pi}\right)^{\frac{3}{2}} l_m \int_0^\infty \frac{(V, l_m) dV e^{-V^2}}{(1 + p^2 l_m^2 / V^2)} \quad . . (12)$$

But this is not the whole current. In the first place there is a polarization current, partly æthereal and partly material, to be added to that of conduction. If  $K$  is the dielectric capacity of the medium, and  $C$  the velocity of light *in vacuo*, the polarization current is

$$i_2 = -(K/4\pi C^2) ipa e^{-ipt}. \quad . . . . (13)$$

Electrons belonging to the atoms, although not free to move through a free path, will also contribute to the current by their vibrations. In so far as they may be paired off with elements of positive electricity into doublets in mean positions, the effect of their vibrations will appear in the material polarization current. This relates to their vibrations within the atom, relatively to one another. We shall suppose that each free electron in the metal necessitates the existence of an unsaturated atom (perhaps, however, shared by several free electrons) with a superabundance of positive electricity equal to the charge on an electron. These extra charges will contribute a current by their vibration, partly within the atom and partly with the atom in its own vibrations as a whole, but since their number is equal to that of the free electrons, the magnitude of their contribution to the current will bear a ratio to the previous conduction current which must be small. For its magnitude cannot exceed that of the ratio of atomic amplitude of vibration to mean free path of an electron. The neglect of this current, in the absence of sympathetic vibrations of the whole unsaturated atom, is therefore valid. But if such vibrations are present this argument fails, and the current thus concerned can be important. Similar considerations apply to the current contribution from bodily convection of the saturated portion of an atom. This must be a true current in an analogous way to the effect, pointed out by Larmor, of translation of a finite part of a moving material system.

But if sympathetic vibrations are present to a certain extent, increasing the atomic amplitude, the uncompensated positive charges may contribute a current

$$i_3 = a (C' + iDp) e^{-ipt}, \quad . . . . (14)$$

where  $(C', D)$  are of like form with  $(A, B)$ ,  $C'$  being unimportant in comparison with  $Dp$ , and both being positive

because proportional to  $e^2$ . Of these magnitudes  $C'$  appears in the absorption due to such vibration, neglected in Schuster's investigation after the manner of Sellmeier, and, in fact, in accordance with custom. But  $Dp$  may be important, and if this occurs, a consideration of  $i_2$  and  $i_3$  shows that it would manifest itself as a change in  $K$ , so that  $K$  is replaced by  $K - 4\pi e^2 D$ . Thus  $K$  would appear to be decreased, and if small, might become a negative quantity. We shall return to this question later, in a comparison with Drude's theory.

If the positive electricity were actually free its effect could be neglected on account of its value of  $e/m$ . Neglecting all effects of this kind, as will be possible usually, we may take as the total current  $i_x = i_1 + i_3$ . This is usually done in the electron theory without question. Thus

$$i_x = (A + ipB - Kip/4\pi C^2) a e^{-ipt} \dots (15)$$

If  $R$  and  $L$  are the equivalent resistance and self-induction of a unit element of the metallic medium, we may also write

$$(R - Lip) i_x = a e^{-ipt} \dots (16)$$

and therefore

$$(R - Lip)^{-1} = A + ipB - ipK/4\pi C^2, \dots (17)$$

from which  $R$  and  $L$  may be determined. These results are of interest in other connexions, and are simple, with the values of  $A$  and  $B$  given later. It is to be noticed that the only ions we have considered are negative electrons, and positive atoms which have lost them.

### *Derivation of Optical Constants.*

Let us consider the propagation of a plane wave in a medium, along a direction  $z$ , the current being along  $x$ . The current  $u$  and electric force  $X$  are related by

$$L du/dt + Ru = X.$$

Moreover,

$$4\pi u = -\partial\beta/\partial z, \quad \dot{\beta} = -\partial X/\partial z.$$

Thus

$$\partial^2 X/\partial z^2 = 4\pi \partial u/\partial t = -4\pi ip X/(R - Lip),$$

or

$$\partial^2 P/\partial z^2 + \theta^2 P = 0, \dots (18)$$

provided that

$$\theta^2 = 4\pi ip (R + Lip)/R^2 + L^2 p^2 = 4\pi^2 (\nu + i\kappa)/\lambda^2, \dots (19)$$

where  $\nu$  and  $\kappa$  are certain optical constants,  $\lambda$  being the

wave-length *in vacuo*. In the metal  $X$  is proportional to the exponential of argument

$$-\frac{2\pi\kappa z}{\lambda} + i\left(\frac{2\pi\nu z}{\lambda} - pt\right), \quad . \quad . \quad . \quad (20)$$

so that  $\nu$  denotes the index of refraction, and  $\kappa$  is a coefficient of extinction, which we may call, after Schuster, the coefficient of optical length. We have the relation

$$\frac{4\pi^2}{\lambda^2} (\nu^2 - \kappa^2 + 2i\nu\kappa) = 4\pi ip (A + ipB - ipK/4\pi C^2).$$

Remembering that  $p = 2\pi C/\lambda$ , this leads to

$$\nu\kappa = \lambda CA, \quad \nu^2 - \kappa^2 = K - 4\pi BC^2, \quad . \quad . \quad . \quad (21)$$

where  $C$  is the velocity of light *in vacuo*, and  $A$  and  $B$  are defined in (12). With  $p=0$  in (11) the conductivity for a steady current is

$$\sigma_0 = 2N \frac{e^2}{m} \left(\frac{q}{\pi}\right)^{\frac{1}{2}} l_m, \quad . \quad . \quad . \quad (22)$$

so that

$$(A, B) = 2q\sigma_0 \int_0^\infty \frac{(V, l_m) dV e^{-qV^2}}{1 + \alpha/qV^2}, \quad . \quad . \quad (23)$$

where

$$\alpha = \pi p^2 m^2 \sigma_0^2 / 4N e^4 = \pi^3 m^2 \sigma_0^2 C^2 / N^2 \lambda^2 e^4, \quad . \quad . \quad (24)$$

and with this value of  $\alpha$ ,

$$\frac{\nu\kappa}{\lambda C} = 2q\sigma_0 \int_0^\infty \frac{V dV e^{-qV^2}}{1 + \alpha/qV^2} \quad . \quad . \quad . \quad (25)$$

$$\nu^2 - \kappa^2 = K - 8\pi q\sigma_0 C^2 l_m \int_0^\infty \frac{dV e^{-qV^2}}{1 + \alpha/qV^2} \quad . \quad (26)$$

The first equation is of course identical with Wilson's equation (5), which he derived from a consideration of heat production.

Wilson gives the second equation without proof, with  $K=1$ , but has dropped a factor  $C^2$  in the last term. A consideration of the dimensions in time of the quantities concerned will justify its presence.

*Reduction of the Integrals.*

Writing  $qV^2 = \omega$  in the first result, we obtain

$$\frac{\nu\kappa}{\lambda C\sigma_0} = \int_0^\infty \frac{\omega d\omega}{\omega + \alpha} e^{-\omega},$$

so that this ratio does not involve  $q$  explicitly, If  $\omega = -\alpha + \zeta$ ,

$$\frac{\nu\kappa}{\lambda C\sigma_0} = e^{-\alpha} \int_\alpha^\infty (1 - \alpha/\zeta) d\zeta e^{-\zeta},$$

or

$$\nu\kappa = \lambda C\sigma_0 (1 - \alpha e^\alpha \text{Ei}(-\alpha)), \quad . \quad . \quad . \quad (27)$$

where  $\text{Ei}(-\alpha)$  is the exponential integral function defined by

$$\text{Ei}(-\alpha) = \int_\alpha^\infty \frac{d\zeta}{\zeta} e^{-\zeta}, \quad . \quad . \quad . \quad . \quad (28)$$

of which exhaustive tables have been constructed by Glaisher\*. If  $\alpha$  is not small, we may write asymptotically

$$\text{Ei}(-\alpha) = e^{-\alpha} \left( \frac{1}{\alpha} - \frac{1}{\alpha^2} + \frac{2}{\alpha^3} - \frac{3}{\alpha^4} \dots \right), \quad . \quad . \quad (29)$$

the series being formally divergent after a certain number of terms, after the usual manner. Taking the first two terms only, as is sufficient for the good conductors, we derive

$$\nu\kappa = \lambda C\sigma_0/\alpha = N^2 \lambda^3 e^4 / \pi^3 m^2 C\sigma_0, \quad . \quad . \quad . \quad (30)$$

this formula being then more accurate than the experimental measures with which it is to be associated.

Under the same circumstances we may expand the second formula, which yields

$$\begin{aligned} \nu^2 - \kappa^2 &= K - 8\pi q^2 \sigma_0 C^2 l_m \int_0^\infty V^2 dV e^{-qV^2} \left\{ \frac{1}{\alpha} - \frac{V^2}{\alpha^2} + \frac{q^2 V^4}{\alpha^3} \dots \right\} \\ &= K - 2\sigma_0 \sqrt{\pi q} C^2 l_m \alpha^{-1} \left( 1 - \frac{3}{\alpha} + \frac{5}{2\alpha^2} \dots \right), \quad . \quad . \quad . \quad (31) \end{aligned}$$

or for good conductors,

$$\nu^2 - \kappa^2 = K - 2\sigma_0 \sqrt{\pi q} C^2 l_m / \alpha = K - \pi m C^2 \sigma_0^2 / \alpha e^2 N, \quad (32)$$

quoting again the value of  $\sigma_0$  in (22).

\* Phil. Trans. 160 A (1870). An abridged form is given in Jahnke & Emde, *Functionentafeln*, Leipzig, 1909.

Determination of  $N$ .

By (30)

$$N^2 = \pi^3 m^2 C \sigma_0 \nu \kappa / \lambda^3 e^4, \quad . \quad . \quad . \quad (33)$$

for metals of sufficient conductivity. By a method of continued approximation we may show, by the series for the exponential integral function, that the more complete formula is

$$N^2 = \pi^3 m^2 C \sigma_0 \nu \kappa \left( 1 + \frac{2\nu\kappa}{\lambda C \sigma_0} + 5 \frac{\nu^2 \kappa^2}{\lambda^2 C^2 \sigma_0^2} \right) / \lambda^3 e^4, \quad . \quad (34)$$

if  $\nu\kappa/\lambda C \sigma_0$  is small enough.

It is more convenient, following Schuster\*, to determine the ratio  $N/n$  of the number of electrons to the number of atoms in a unit of volume. If  $\rho$  be this ratio, and  $V$  the atomic volume of the metal,

$$\frac{m}{Ne^2} = 5.6 \cdot 10^{-12} \frac{V}{\rho}, \quad . \quad . \quad . \quad (35)$$

where the value  $1.86 \cdot 10^7$  has been used for  $e/m$ , and the ratio of the weight of a hydrogen atom to the charge  $e$  is quoted from electrolytic measurements as  $1.04 \cdot 10^{-4}$ . Thus

$$\rho^2 = 31.4 \cdot 10^{-24} V^2 \frac{\pi^3 \sigma_0 C}{\lambda^3} \nu \kappa \left( 1 + \frac{2\nu\kappa}{\lambda C \sigma_0} + \frac{5\nu^2 \kappa^2}{\lambda^2 C^2 \sigma_0^2} \right). \quad (36)$$

Higher powers in the bracket will not be required. For lead and sodium light, the most unfavourable case worked out below,  $\nu\kappa/\lambda C \sigma_0$  becomes .08, and for nickel it is .04.

Schuster's formula is equivalent to

$$\rho^2 = 31.4 \cdot 10^{-24} V^2 \frac{4\pi^2 \sigma_0 C}{\lambda^3} \nu \kappa \left( 1 + \frac{\nu\kappa}{\lambda C \sigma_0} \right), \quad . \quad (37)$$

where the bracket is not approximate in this case. For metals of high conductivity the ratio of the values of  $\rho^2$  from the two formulæ is merely  $\pi/4$ , Schuster's formula giving the higher value.

The assumption of equal velocities of agitation for all the electrons is known to give good general accord in most respects with experiment, so that the closeness of the values of  $\rho$  from the two velocity laws is not surprising.

But it seems that, on general grounds, we may expect one of these laws to give a better approximation to the truth. For in reality the atoms do move, and the electrons collide with one another. This must cause Maxwell's law to be

\* *L. c.* p. 152.

approximately fulfilled, and to be a fair representation of the actual state of things, if the mean free path is properly interpreted.

The fact that difficulties have been suggested in the theory of emission of light from metals is not relevant to the present purpose, for, as Wilson has foreseen, it is probable that Jeans's formula for radiation, based on the hypothesis of equal velocities of agitation, would be obtained exactly if the influence of electronic collisions with one another and with atoms were properly accounted for, even with the Maxwellian velocity distribution. That these collisions are negligible, in a certain sense, in the theory of conduction does not necessarily render them so in that of radiation. But it may be shown in fact, that even neglecting these collisions, a very close approximation to Jeans's formula is found in most cases, so that these suggested difficulties are almost non-existent. But we may leave this matter now, as it is foreign to our present inquiry.

Let us now consider Schuster's values of  $N$  in detail. Neglecting the term in the bracket, as is lawful for all metals whose conductivity is greater than that of lead,

$$\rho^2 = 31 \cdot 4 \cdot 10^{-24} V^2 \frac{4\pi^2 \sigma_0 C}{\lambda^3} \nu \kappa, \quad . \quad . \quad . \quad (38)$$

and with  $C = 3 \cdot 10^{10}$ , and  $\lambda = 5 \cdot 89 \cdot 10^{-5}$  for sodium light, this yields

$$\rho^2 = 183 V^2 \sigma_0 \nu \kappa \cdot 10^{-5}; \quad . \quad . \quad . \quad . \quad (39)$$

Schuster gives

$$\rho^2 = 45 \cdot 6 V^2 \sigma_0 \nu \kappa \cdot 10^{-5}, \quad . \quad . \quad . \quad . \quad (40)$$

and has apparently dropped a factor 4, for this is exactly 1/4 of our result. The values of  $\rho$  given in his table therefore require multiplication by 2. In the case of certain metals, a calculation from Drude's constants gives different values for  $\nu \kappa$ , the metals concerned being silver, gold, and copper. For silver we find  $\cdot 66$  for  $1 \cdot 66$ , for gold  $1 \cdot 03$  for  $2 \cdot 06$ , and for copper  $1 \cdot 68$  for  $1 \cdot 60$ .

Schuster's calculation has been repeated, with the adoption, however, in possible cases, of the now accepted measurements of conductivity of Jäger and Diesselhorst\*, as the most accurate. They are the values of the conductivities at  $18^\circ \text{C}$ . The results of this repeated calculation are shown in Table I., the complete formula (37) being used in necessary cases. For cobalt, antimony, magnesium, and lead the conductivities are taken from Schuster's table.

\* *Wissen. Abhand. der Physikal. Techn. Reichsanstalt*, iii. p. 269 (1900).

TABLE I.

METAL.	V.	$10^5 \sigma_0$ .	$\nu\kappa$ .	$\rho^2$ .	$\rho$ .
Nickel .....	6.7	8.5	5.94	4.316	2.07
Mercury.....	14.8	1.044	8.58	5.260	2.29
Bismuth.....	21	0.84	6.95	6.921	2.63
Cobalt .....	6.7	9.92	8.54	7.293	2.70
Silver .....	10.3	61.4	6.64	7.915	2.81
Copper .....	7.1	57.2	1.68	8.860	2.98
Gold .....	10.2	41.3	1.03	8.115	2.85
Magnesium ...	13.3	23.7	1.65	12.65	3.56
Platinum .....	9.1	9.24	8.78	12.29	3.50
Lead .....	18.2	5.1	6.995	23.29	4.83
Cadmium .....	13.0	13.13	5.66	22.99	4.79
Antimony .....	17.9	2.8	15.02	32.16	5.67
Tin .....	16.2	8.28	7.77	30.90	5.56
Zinc .....	9.5	15.83	11.62	30.38	5.51
Aluminium ...	10.1	31.6	7.53	44.43	6.66

We notice that the order of two metals in that table is sometimes reversed. Thus the theory of equal velocities of agitation of electrons leads to values of  $\rho$  ranging not from 1 to 3, but from 2 to nearly 7. They are never less than 2.

For sodium light the formula (36) becomes

$$\rho^2 = 143 V^2 \sigma_0 \nu \kappa \left( 1 + \frac{2\nu\kappa}{\lambda C \sigma_0} + \dots \right). \quad (41)$$

In Table II. the values of  $\rho^2$  and  $\rho$  calculated from this formula are given. Mercury, antimony, and bismuth are omitted, as they have a value of  $\nu\kappa/\lambda C \sigma_0$  too great for the initial convergence of the formula. For mercury this value is .465, for antimony .303, and for bismuth .469. These cases necessitate the use of tables of the exponential integral function.

TABLE II.

METAL.	$\rho^2$ .	$\rho$ .	METAL.	$\rho^2$ .	$\rho$ .
Nickel.....	3.499	1.87	Platinum .....	9.602	3.10
Cobalt .....	5.982	2.45	Lead .....	20.11	4.48
Silver .....	6.185	2.49	Cadmium .....	17.96	4.24
Copper .....	6.923	2.63	Tin.....	24.145	4.92
Gold .....	6.341	2.52	Zinc .....	23.74	4.87
Magnesium ...	9.886	3.14	Aluminium ...	34.72	5.89

The range of values of  $\rho$  is nearly the same as before, but no value exceeds 6. The general agreement of the two values for any metal admits, at this stage, of the statement that the number of free electrons in a metal can be fairly accurately known under the conditions which have been assumed, namely, that the temperature is about  $18^\circ \text{C}$ ., and that a periodic force, whose frequency is that of sodium light, acts on the metal.

We now proceed to another aspect of the subject, based on the equation (32), and for this purpose we calculate certain optical constants of the metals from the experimental measurements of Drude.

The experiments of Drude \* on the optical constants of the metals were very exhaustive, and the results obtained were, for series of determinations with the same metal, remarkably in accord. A critical study of Drude's results has convinced the writer that the error in certain sets of entries in Drude's tables can rarely be greater than about one per cent., and that in the results of these experiments we have a means of obtaining much more definite information, concerning the atoms of metals, than has been attempted hitherto. The only possible error is apparently a systematic one throughout the results, and this does not seem likely to occur.

Drude uses two constants  $n$  and  $\chi$ , where  $n$  is the index of refraction of the metal and is identical with  $\nu$ . The relation between  $\kappa$ , the coefficient of optical length, and Drude's  $\chi$  is embodied in

$$\nu + i\kappa = n(1 + i\chi), \quad \dots \dots (42)$$

so that  $\nu = n$ , and  $\kappa = n\chi$ . Thus  $\nu\kappa = n^2\chi$ , and  $\nu^2 - \kappa^2 = n^2(1 - \chi^2)$ . The value of  $\nu\kappa$  has appeared already in the first table, but it is convenient to repeat it below. In the case of sodium light, the values of these constants are exhibited below, the first columns being taken from Drude's paper. The values for cobalt are taken from a later paper †, as Drude made it the subject of a special examination.

The formula (32) becomes, to a higher order,

$$K + \kappa^2 - \nu^2 = \frac{\pi m C^2 \sigma_0^2}{\alpha N e^2} \left( 1 - \frac{3}{\alpha} + \frac{5}{2\alpha^2} - \dots \right).$$

The first approximation to  $\alpha^{-1}$  or  $\pi^3 m^2 \sigma_0^2 C^2 / N^2 \lambda^2 e^4$  is  $\nu\kappa / \lambda C \sigma_0$  by (30), and the second is

$$\frac{\nu\kappa}{\lambda C \sigma_0} \left( 1 + \frac{2\nu\kappa}{\lambda C \sigma_0} \right),$$

\* Wied. *Ann.* xxxix. p. 537.

† Wied. *Ann.* xlii. p. 189.



TABLE III.

METAL.	$n$ or $\nu$ .	$\chi$ .	$\kappa$ .	$\nu\kappa$ .	$\kappa^2 - \nu^2$ .
Nickel .....	1.79	1.86	3.32	5.94	7.88
Mercury.....	1.73	2.87	4.96	8.58	21.61
Bismuth.....	1.90	1.93	3.66	6.95	9.84
Cobalt .....	2.12	1.90	4.03	8.54	11.75
Silver.....	.181	20.2	3.67	.664	13.33
Copper .....	.641	4.03	2.62	1.68	6.43
Gold .....	.366	7.70	2.82	1.03	7.81
Magnesium ...	.373	11.8	4.42	1.65	19.23
Platinum .....	2.06	2.06	4.26	8.78	13.77
Lead .....	2.01	1.73	3.48	6.995	8.05
Cadmium .....	1.13	4.43	5.01	5.66	23.82
Antimony .....	3.04	1.63	4.94	15.02	15.26
Tin .....	1.48	3.55	5.25	7.77	25.41
Zinc .....	2.12	2.60	5.48	11.62	25.89
Aluminium ...	1.44	3.64	5.23	7.53	25.40

so that on reduction

$$K + \kappa^2 - \nu^2 = \frac{Ne^2\lambda^2}{\pi^2 m} \left(1 - \frac{\nu\kappa}{\lambda C\sigma_0}\right). \quad (43)$$

Writing as before,  $V$  being the atomic volume, and  $\rho$  the ratio of the number of free electrons to the number of atoms,

$$\frac{m}{Ne^2} = 5.6 \cdot 10^{-12} \frac{V}{\rho},$$

then

$$\rho = 5.6 \cdot 10^{-12} \frac{\pi^2 V}{\lambda^2} (K + \kappa^2 - \nu^2) \left(1 + \frac{\nu\kappa}{\lambda C\sigma_0}\right), \quad (44)$$

where for good conductors, the last bracket is unity. In the case of sodium light

$$\rho = 15.59 \cdot 10^{-3} V (K + \kappa^2 - \nu^2) \left(1 + \frac{\nu\kappa}{\lambda C\sigma_0}\right). \quad (45)$$

Consider now the formula to which the hypothesis of equal velocity of agitation would lead. Quoting Schuster\*, we have, in our present notation,

$$\nu^2 - \kappa^2 = K - 4\pi\sigma_0^2 C^2(\sigma)/(1 + \sigma_0^2 p^2(\sigma)^2), \quad (46)$$

\* *L. c.* p. 154.

where ( $\sigma$ ) denotes  $m/Ne^2$ , and unity may be neglected in the denominator for good conductors. When this is neglected we obtain

$$\nu^2 - \kappa^2 = K - Ne^2\lambda^2/m\pi,$$

and finally

$$\rho = 5.6 \cdot 10^{-12} \frac{\pi V}{\lambda^2} (K + \kappa^2 - \nu^2), \quad . \quad . \quad . \quad (47)$$

which is less than the value of  $\rho$  in (44) by a factor  $\pi$ . For a given value of the dielectric capacity, accordingly, this theory leads to a value of  $\rho$  only about a third of that of the foregoing. We shall return to this formula shortly.

There is a tendency, exemplified in Wilson's paper, to suppose that  $K$  may be written equal to unity for a metal, so that the polarization current is entirely æthereal. This cannot be correct. Let us examine the value to be attached to  $K$  in order that the formula (44) shall give the same value of  $\rho$  as we found before.

In the first place, we calculate  $\rho$  on the basis  $K=1$ , in order to see how far this assumption fails. The formula used is (44) and the results are exhibited in Table IV. The value thus calculated is called  $\rho_1$  and is placed beside  $\rho$ .

TABLE IV.

METAL.	$\rho_1$ .	$\rho$ .	K.	METAL.	$\rho_1$ .	$\rho$ .	K.
Nickel .....	·986	1·87	8·96	Platinum ...	2·14	3·10	7·59
Cobalt .....	1·43	2·45	10·06	Lead .....	2·84	4·48	6·26
Silver .....	2·35	2·49	1·81	Cadmium ...	5·15	4·24	-3·38
Copper .....	·84	2·63	16·82	Tin .....	6·82	4·91	-6·39
Gold .....	1·43	2·52	7·68	Zinc .....	4·07	4·87	6·27
Magnesium .	4·29	3·14	-4·41	Aluminium .	4·25	5·89	11·18

The values of  $K$ , the dielectric capacity required to give the value of  $\rho$  derived from Table II., are shown in the third columns of the above table. They are calculated from the formula

$$K + \kappa^2 - \nu^2 = (\kappa^2 - \nu^2) \rho / \rho_1, \quad . \quad . \quad . \quad (48)$$

which follows immediately from (45) by the definition of  $\rho_1$ .

Of these values of  $K$  three are negative, but small. The range of the positive values of  $K$  is also small, and there is no positive value which is unduly large in comparison with known values for non-metallic elements. Thus, for example, carbon, in the form of diamond, has a refractive index equal

to 2.44, and writing  $K=n^2$ , this should involve a dielectric capacity of 5.9, of like magnitude with all the values in the table. But no element is known with a dielectric capacity, as deduced from the refractive index, greater than about this magnitude. We note that  $K$  is the dielectric capacity for *steady* currents, if the moving ions are all electrons.

A mode in which negative values of  $K$  might arise has been suggested in (14). If this be the cause in the case of tin, magnesium, and cadmium, the effect concerned is not large, for the negative values are small. We may therefore, apparently, still rely upon the estimates of  $\rho$  given by the first equation, the absorption of selective type being very small. But it must be admitted at this stage that the Maxwellian hypothesis has given an excellent account of Drude's experiments in so far as we have considered them. The agreement is very exact, for a small divergence from this law can, as we shall see, produce a great change in the necessary value of  $K$ . It would seem that the value of  $K$  is capable of deciding between the hypotheses, and of determining the exact extent to which any hypothesis is correct, and if this be granted, we may claim to have shown that the formulæ developed in this paper are mathematically sufficient, within the limits of experimental error, to account for the optical behaviour of all these metals in sodium light.

Before proceeding to examine the results of the other hypothesis, let us consider what the limits of experimental error probably are. For an analysis of Drude's results may be pushed further, and yields very profitable conclusions. In several cases, for example, silver, he has given the results of several experiments performed on the same metal, prepared in different ways. Thus for silver we have the following particulars:—

(1) For silver made solid by pressure,

$$n\chi=3.65, \quad n=.169, \quad \chi=21.7.$$

(2) For silver deposited by electrolysis from the double cyanide of silver and potassium,

$$n\chi=3.62, \quad n=.170, \quad \chi=21.2.$$

(3) For silver chemically prepared from the pure nitrate,

$$n\chi=3.69, \quad n=.206, \quad \chi=18.0.$$

(4) For the chemically prepared silver, after heating,

$$n\chi=3.71, \quad n=.180, \quad \chi=20.6.$$

The mean of all the experiments is

$$n\chi=3.67, \quad n=.181, \quad \chi=20.2.$$

Thus we see that the greatest range of variation in  $n\chi$  is .09 in 3.67, so that the error in the mean value can hardly exceed about one per cent. at most. The greatest range in  $\chi$  is 37 in 181, or one in five, so that this error can be ten per cent. Thus the value of  $n$  is not trustworthy to the same extent as that of  $n\chi$ .

Silver is the metal which Drude has examined most exhaustively, but the same remarks apply to the others, and the accuracy of  $n\chi$  is always equally certain, in cases where the observations given are sufficient to test it, whereas it is possible for  $n$  in some cases to be incorrect by about 10 per cent. for certain metals on which fewer observations were made. Thus  $\kappa^2 - \nu^2$ , which we have calculated from Drude's results, is liable to the same percentage error as  $n^2$ , and this can be 20 per cent. in the most unfavourable case, but will not be, for the majority of metals, of any such magnitude.

It may be shown that the existence of such an error would reverse the sign of  $K$  for cadmium, and would nearly do so for tin and magnesium. We notice this point, although inclining to the belief that the values of  $K$  for these metals are a result of sympathetic vibration. Some grounds for this belief will appear in a subsequent paper.

It is, however, worthy of notice that Drude himself expresses some doubt as to the accuracy of the value of  $n$  for magnesium, for the specimen used became impure and was difficult to deal with. In the case of cadmium, only one set of experiments appears to have been made, and no comments are given concerning it. Tin is a metal of a pronounced crystalline structure, and this influence may be suggested in its case. The experiments made with it agree very well among themselves, and they seem to the writer to be as accurate as for most metals. Although no statement is made to that effect, it is probable that some precautions were taken against this, for they were in the case of copper, in which results are given both for doubly refracting and for isotropic copper. The calculations of a later paper, which may be mentioned now, will indicate that the constants for tin, and the value of  $\rho$  to which they lead, are in accord with others.

We have seen, therefore, that the greatest experimental error likely in  $\nu\kappa$  or  $n^2\chi$  is ten per cent. at most. That of  $\sqrt{\nu\kappa}$  cannot therefore exceed about 4 per cent., and this will be the error in  $N$  or  $\rho$  at most, when calculated from the proper velocity distribution.

Errors in  $\sigma_0$  have been reduced to a minimum by taking

its value at  $18^{\circ}\text{C.}$ , a temperature which cannot have been far from that of the surroundings in Drude's experiments. The temperature coefficient of the conductivity is also very small. We may conclude, finally, that when the proper law of velocities is used in the calculation, the value of  $\rho$  calculated from  $\nu\kappa$  will only have a possible error of 4 or 5 per cent.

Consider now the values of  $\rho_1$  and  $K$  furnished by the equal velocity hypothesis. In the following table some of these are calculated from the formula (47), the best conductors being selected for convenience of calculation.

TABLE V.

METAL.	$\rho_1$ .	$\rho$ .	K.	METAL.	$\rho_1$ .	$\rho$ .	K.
Nickel .....	302	2.07	60.92	Platinum ...	681	3.50	60.24
Cobalt .....	427	2.70	80.57	Cadmium ...	1.64	4.79	45.84
Silver .....	748	2.81	38.65	Tin .....	2.17	5.56	38.92
Copper .....	267	2.98	75.51	Zinc .....	1.29	5.51	85.06
Gold .....	455	2.85	46.21	Aluminium .	1.35	6.66	101.3
Magnesium .	1.36	3.56	31.01				

This table appears to be decisive between the two alternatives. The values of  $K$  just calculated are too large to be accepted. An approximate calculation for the other metals shows that they furnish no exception to this statement.

When these values are regarded side by side with those of Table IV. it seems that we may conclude, with some certainty, that only the Maxwellian distribution of velocities can be admitted, and that it suits the facts very well, and so well that we may proceed further with our conclusions. A very small deviation from this law in the direction of that of equal velocity would cause a rapid increase in the necessary value of  $K$ . The figures for silver, the subject of the most careful experiments, are very convincing as regards the perfectly satisfactory nature of the selected law.

Our ultimate conclusion is, accordingly, that the values of  $\rho$  in Table II. cannot, in the most unfavourable cases, with the possible exception of tin, magnesium, and cadmium, differ from the true values by more than about 5 per cent. But when these numbers are examined, it is seen that, except in the case of cadmium, they are all very close to integers or

half integers. In the following table the nearest integer, and the percentage difference from it, is shown in each case.

TABLE VI.

METAL.	$\rho$ .	Nearest semi-integer.	Per cent. difference.	METAL.	$\rho$ .	Nearest semi-integer.	Per cent. difference.
Nickel .....	1.87	2	6.5	Platinum ...	3.10	3	3.3
Cobalt .....	2.45	$2\frac{1}{2}$	2	Lead .....	4.48	$4\frac{1}{2}$	0.44
Silver .....	2.49	$2\frac{1}{2}$	0.4	Cadmium ...	4.24	4 or $4\frac{1}{2}$	—
Copper .....	2.63	$2\frac{1}{2}$	5.2	Tin .....	4.92	5	1.6
Gold .....	2.52	$2\frac{1}{2}$	0.8	Zinc .....	4.87	5	2.6
Magnesium .	3.14	3	4.66	Aluminium .	5.89	6	1.8

Now the percentage difference between successive half integers is  $8\frac{1}{2}$ , even for the case of aluminium. For nickel, which gives an apparently large difference, the percentage from the half integer on the other side is about 20. Our differences are all very small, and *they are always within the experimental limit of accuracy*. The only exception is cadmium, and in this case it is significant that  $\rho=4.24$ , or exactly a quarter of an integer.

The closeness of the value for silver to  $2\frac{1}{2}$  is very striking, especially when its behaviour in other respects is taken into account, together with the detail of Drude's experiments with it.

It is not proposed to say more about these numbers at present, as the results of another paper, shortly to be published, on the dispersion of light by metals, confirm these results in some detail. But it would appear that the exact number of free electrons per atom in a metal can be found, and results obtained which may tend towards a comprehension of the structure of the atoms of the elements.

It is evident that the assumption of a dielectric capacity of 1.8, and of five free electrons for every two atoms of silver, gives a mathematically precise account of its behaviour towards sodium light. We shall afterwards prove that the same assumptions can explain its behaviour towards red light. Drude's theory does not lead to conclusions so exact, although these conclusions are a complete vindication of the ideas from which Drude started. His experimental results are fundamental to the conclusions.

It is to be noted that the actual value of  $\rho$  is proportional inversely to the assumed value of  $e/m$  for the negative

electrons in solids, but that the value of  $K$  derived is independent of this ratio, as may be shown on reference to the formulæ. We have used the value  $e/m = 1.86 \cdot 10^7$ . Drude was of the opinion that the proper value was  $1.5 \cdot 10^7$  for the electrons in solids. But it has seemed preferable to select the other value. Prof. O. W. Richardson, by a beautiful series of experiments, has established the nature of the ions emitted by hot bodies, and accepting his view that the negative ions are the negative electrons of conduction which have escaped from the forces retaining them in the metal, it is necessary to take a value higher than this, Prof. Richardson's standard value being  $1.88 \cdot 10^7$ . We may say that no other value generally accepted for  $e/m$  leads to values of  $\rho$  so conclusive as those of the last table.

A brief recapitulation of the other assumptions may be desirable. In the first place we have supposed that the carriers of electricity are negative electrons and not ions. Moreover, the free positive electricity remains fixed to the atom, and can only move by vibration with it. If the vibrations are not sympathetic the motion of the positive electricity and of the atoms containing it may be neglected, but if they are the amplitude of vibration may be large, and thereby an apparently negative value of  $K$  may be produced by ignoring it. A negative value of  $K$  denotes the presence of such vibrations, which, of course, cannot be predicted from the absorption spectrum of the vapour of the metal, in which the aggregates of atoms forming the molecules will be different. If the negative value of  $K$  is small the calculation of  $\rho$  by the method given will not be seriously affected. Vibrations of the saturated portion of an atom which has lost electrons will obey, for internal vibration in the atom, the laws of material polarization in doublets, and if the convection of these doublets is not too large, may be ignored except in the contribution to the dielectric capacity. On this basis the optical constants may be found for a given law of velocity among the electrons, and it is found possible to discriminate between such laws in complete favour of that of Maxwell, which is found to lead to results of definitely close agreement with experiment. It may be claimed that this treatment is more satisfactory, in that it is less vague than, for example, that of Drude, which involves an introduction of frictional forces whose origin is difficult to interpret. It would seem, also, that negative electrons and unsaturated atoms caused by their escape, are the only entities which ought to be admitted. Richardson's experiments appear to the writer to prove that other ions are not present in metals, for he has

shown fairly definitely that the negative ions emitted by hot metals are electrons, and that positive ions emitted even by alkaline sulphates and fluorides are atoms of the metallic base which have lost electrons\*.

Finally, a few remarks must be made as to the significance of  $K$ , and this may be most conveniently done by a comparison with the theory as set forth in Drude's treatise. This theory divides the current into three portions, (1) Æthereal polarization current, (2) Current carried by positive ions, and (3) Current carried by negative ions. These ions, positive or negative, may be of more than one "class." Equations of motion of these classes are given in a form which is unsatisfactory in its introduction of a viscous frictional term. When there are only two classes, one of negative electrons moving freely and one of positively charged ions with a natural period of their own, Drude gives, in terms of the constants ( $\nu$ ,  $\kappa$ ) we have used,

$$\nu^2 - \kappa^2 = 1 + \frac{\mathfrak{S}}{1 - (t_1/t)^2} - \frac{4\pi N m}{e^2(r^2 + m^2/t^2 e^4)}$$

$$\nu\kappa = \frac{2\pi t r N}{r^2 + m^2/t^2 e^4},$$

where, if a group  $dN$  of electrons can be held to constitute a class, and if the frictional coefficient  $r$  is otherwise interpreted, the value of  $\nu\kappa$  and the last term of  $\nu^2 - \kappa^2$  become, on summation by Maxwell's law, identical with the values we have used.

Drude's  $\mathfrak{S}$  is a positive constant determining the force of restitution of an ion when it vibrates under the action of the electric force,  $t_1$  is the natural period of the ion, and  $t$  that of the light. Thus the sympathetic vibration of an atom affects this term. If it is important the denominator is affected, and  $\nu\kappa$  is altered to a smaller extent in consequence of the resulting absorption. This alteration is relatively unimportant if  $t_1$  is not nearly equal to  $t$ .

The current analysis above is not complete. Vibrations will take place ordinarily within the atom, and they will include the vibrations of doublets in which the positive and negative charges approach and recede. If  $d$  is a component of their distance apart, along any direction, a polarization current  $\sum ed$  is formed in that direction, the summation being for all doublets in a unit volume. The convection of such polarization is also effective to some extent. It will not be correct, in such a case, to suppose that in a non-metallic

\* *Vide* Phil. Mag. December 1910.



body the dielectric capacity observed for non-oscillatory forces will be  $1 + \sum \mathfrak{S}$ , the summation being for all kinds of ions in the substance, so that  $\mathfrak{S}_r$  may be called the dielectric capacity of an ion of type  $r$ . This is done, for example, by Drude, who thus arrives at the definition of ordinary dielectric capacity as the sum of the capacities of the free æther and of all the types of ions.

A more correct formula must be  $K_1 + \sum \mathfrak{S}$ , where  $K_1$  is different from unity, and may be more important than  $\sum \mathfrak{S}$ . It is an effect of material polarization in doublets. Calculations of  $\mathfrak{S}$  from the known positions of absorption of such bodies may therefore be subject to error. According to some views atomic doublets are rigid, and can only move as a whole, say by twisting round, the positive and negative charges preserving their distance apart. Sir J. J. Thomson has suggested the use of such doublets in a recent paper on the theory of radiation\*.

But whatever  $K_1$  may be, the quantity  $K$  which we have employed denotes  $K_1 + \mathfrak{S}/(1 - (t_1/t)^2)$ , which in the case of non-periodic forces becomes  $K_1 + \mathfrak{S}$ , where  $\mathfrak{S}$  relates to the positively charged atom only, whose free period is  $t_1$ . The negative electrons have been accounted otherwise. For steady forces  $K_1 + \mathfrak{S}$  for this atom cannot be very different from the kind of value it may have in the case of non-metallic elements, that is to say, it may range perhaps from 1 to 20. Now  $K$ , when the force is periodic, differs from  $K_1 + \mathfrak{S}$  by an additive amount  $\mathfrak{S}t_1^2/(t^2 - t_1^2)$ . But many free vibrations of a metallic atom must, on most theories, be far down in the infra-red, so that when  $t$  is a period in the visible spectrum, this additive amount is negative, and thus  $K$  is less than  $K_1 + \mathfrak{S}$  for periodic forces in the visible spectrum. Thus our magnitude  $K$  is more certain than  $K_1 + \mathfrak{S}$  not to exceed, say, 20 at most, and may in some cases be negative if  $t_1$  is nearer to  $t$  than usual, or if  $\mathfrak{S}$  is larger.

It is evident from this reasoning that the values of  $K$ , to which we are led by the theory of equal velocity of agitation of the free electrons, cannot be admitted, and that a method of discrimination between hypotheses of velocity has been found. The nature of the values given by the use of Maxwell's law is exactly what it ought to be, and so exact that it became possible to credit the law with a very high degree of accuracy. On this basis it is found that the description of the behaviour of the various metals in yellow light is very complete, and, as stated, in a later paper it will be shown that the description is equally good for other frequencies.

\* Phil. Mag. July 1910.

We can then proceed to more elaborate deductions, and arrive at the results of the last table. These results are of course tentative in so far as integers are invoked. For example, in the case of magnesium, we found  $\rho = 3.14$ , the nearest integer being 3, and within the limit of experimental error. We showed that there is nothing, from the optical point of view, against the hypothesis that an atom of magnesium has exactly three electrons free. But  $3.14 \times 7$ , for example, is 22 almost exactly, and as this value may be exact, if the experiments are, it is possible that a solid magnesium molecule contains 7 atoms, and has 22 electrons to spare. Such aggregates of atoms are of course to be expected. Sir J. J. Thomson, in his recent paper on rays of positive electricity\*, has found some complex aggregates even in gases and vapours, of which we may mention the polymer  $O_6$  of oxygen, with a positive charge, and also a ray of an electric atomic weight of 800 in mercury vapour, which can be explained as an aggregate of four atoms of mercury with only one negative electron missing.

Information as to the presence of these aggregates can be obtained by measuring the optical constants of fused metals. In the process of fusion dissociation of these aggregates will usually occur, and a different value of  $\rho$  would be found for the liquid. Experiments on these lines would be very valuable.

[*Note added June 28th.*] While this paper is in proof, my attention has been directed to a paper by B. J. Spence, in which Drude's values of  $n$  for gold, silver, and platinum are questioned. This paper will be discussed later.

## XXVII. *Note on the Optical Properties of Fused Metals.*

By J. W. NICHOLSON, M.A., D.Sc.†

IN the preceding paper, concerned with the effective number of free electrons in an atom of a metal, it was suggested that a determination of the optical properties of metals in the liquid state would afford valuable evidence of changes in the state of molecular aggregation during the process of fusion.

The only metal for which such experiments have been made appears to be tin, which was examined by Drude in his paper of 1900‡.

\* Phil. Mag. February 1911.

† Communicated by the Author.

‡ *Annalen der Physik*, Band xxxix.

Owing to lack of knowledge of the electrical conductivity of this metal in the liquid state, it was not possible to utilise the results of these experiments in the earlier paper.

It appears, however, that the conductivity has been determined by Vassura. The result is quoted, without the precise reference, by W. Williams\* in the course of a valuable summary and discussion of the experimental work which has been done in connexion with changes of resistance due to temperature.

According to Vassura, the ratio of the resistivity just after fusion to that just before is, for tin 2.1, and for cadmium 2.3.

De la Rive has given the corresponding ratios for two other metals, zinc 2.0, and lead 1.9.

The optical constants are known only for the case of tin, in sodium light. In the notation of the earlier paper, Drude gives

$$n=2.10, \quad \chi=2.15,$$

so that

$$\nu=2.10, \quad \kappa=4.50, \quad \nu\kappa=9.45, \quad \kappa^2-\nu^2=15.8,$$

where  $\nu$  is the index of refraction, and  $\kappa$  the coefficient of optical length.

According to Vicentini and Omodei's measurements, the density of the liquid metal is 6.988, and its atomic weight being 119.0, the atomic volume of the liquid becomes 17.0.

For the calculation, from the optical constants, of the effective number of free electrons in an atom, we require the conductivity of the liquid, in absolute measure, at the melting-point, which is 230° C.

If  $u$  denotes the ratio of the resistance at  $t^\circ$  C. to that at 0° C., Fleming and Dewar's measurements for tin give

$$\frac{du}{dt} = .00425 + .0000040 t,$$

from which

$$(\text{Resistance at } 230^\circ \text{ C.})/(\text{Resistance at } 0^\circ \text{ C.}) = 2.083,$$

and

$$(\text{Resistance at } 18^\circ \text{ C.})/(\text{Resistance at } 0^\circ \text{ C.}) = 1.077.$$

Thus the conductivity just before fusion is

$$\sigma' = 8.28 \cdot 10^{-5} \times 1.077/2.083 = 4.28 \cdot 10^{-5},$$

where the ordinary value of the conductivity at 18° C. has been used.

\* Phil. Mag. May 1902, p. 515.

By Vassura's result, the conductivity after fusion, for steady currents, is

$$\sigma_0 = \sigma' / 2 \cdot 1 = 2 \cdot 04 \cdot 10^{-5}.$$

In the case of sodium light, the formula (41) of the other paper for the number,  $\rho$ , of free electrons per atom is

$$\rho^2 = 143 V^2 \sigma_0 \nu \kappa \cdot 10^{-5},$$

and if  $K$  be the dielectric capacity, we have in addition

$$\rho = 15 \cdot 59 V (K + \kappa^2 - \nu^2) \cdot 10^{-3}.$$

If  $\rho_1$  is the value furnished by writing  $K=1$ , we find with the present values,

$$\rho = 2 \cdot 85, \quad \rho_1 = 4 \cdot 56.$$

The value of  $K$  required to bring these to equality is  $-5 \cdot 32$ , so that we may infer the presence of sympathetic vibration in the liquid also.

In a later paper, it will be shown that there is some reason for the conclusion that tin is a metal in which higher frequency of the vibrations may cause the liberation of more electrons, and that in a case of this kind, the true number of free electrons for a *steady current* is  $\rho^2/\rho_1$ , combined with a value of  $K$  positive and nearly unity.

For solid tin this becomes  $3 \cdot 54$ , and for the liquid  $1 \cdot 78$ . It is, perhaps, significant that one of these values is almost exactly half the other, and a simple dissociation of atomic aggregates in the process of fusion is suggested.

## XXVIII. On the Latent Heat of Vaporization of Liquids.

By WM. C. McC. LEWIS, M.A., D.Sc., *Physical Chemistry Laboratory, University College, London* \*.

THE quantity of heat added to any system is expressed usually as follows :

$$dQ = C_v dT + l dv, \quad V \quad K \quad H$$

where  $C_v$  denotes the specific heat of the system at constant volume and  $l$  the 'latent heat of expansion,' *i. e.* the heat required to keep the temperature constant while the expansion takes place. Also the change in total energy  $dU$  of the system may be written

$$dU = dQ - p dv,$$

where  $p$  denotes the external pressure to which the system is subjected.

\* Communicated by the Author.

Combining both equations one obtains

$$dU = C_v dT + (l - p)dv.$$

Further, if the change is a reversible one, the increment of entropy may be expressed

$$d\phi = \frac{C_v dT}{T} + \frac{l}{T} dv.$$

Since  $dU$  and  $d\phi$  are complete differentials it follows that

$$\frac{\partial C_v}{\partial v} = \frac{\partial l}{\partial T} - \frac{\partial p}{\partial T}; \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and also

$$\frac{1}{T} \frac{\partial C_v}{\partial v} = \frac{1}{T} \frac{\partial l}{\partial T} - \frac{l}{T^2},$$

or

$$\frac{\partial C_v}{\partial v} = \frac{\partial l}{\partial T} - \frac{l}{T} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence from (1) and (2) we obtain the usual expression

$$l = T \left( \frac{\partial p}{\partial T} \right)_v.$$

The same expression may be obtained in the case of a liquid by applying van der Waals' equation, and also by introducing a modified form of Dupré's relation between the internal pressure  $K$  of the liquid and the latent heat of vaporization  $l$  per unit volume of the liquid. Thus, writing van der Waals' equation in the form

$$p = \frac{RT}{v-b} - K,$$

one obtains on differentiating with respect to  $T$ , keeping the volume constant,

$$\frac{\partial p}{\partial T} = \frac{p + K}{T} - \frac{\partial K}{\partial T},$$

or

$$T \frac{\partial p}{\partial T} = K - T \frac{\partial K}{\partial T},$$

in which  $p$  is neglected compared with  $K$ .

Now if we write (*cf.* "Note on the Internal Pressure of a Liquid," *Phil. Mag.* July 1911)

$$K - l = T \frac{\partial K}{\partial T},$$

one obtains as before

$$l = T \frac{\partial p}{\partial T}^*.$$

Further, since

$$\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T = -1,$$

we obtain

$$l = -T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T = -\frac{T \left(\frac{\partial v}{\partial T}\right)_p}{\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T} = -T \frac{\alpha_1}{\beta}.$$

where  $\alpha_1$  = the coefficient of expansion of the liquid with temperature;

$\beta$  = the coefficient of compressibility of the liquid at constant temperature.

Further, if  $\rho$  is the density of the liquid at the temperature in question, the latent heat of vaporization  $L$  per gram may be written

$$L = -\frac{T \alpha_1}{\rho \beta}.$$

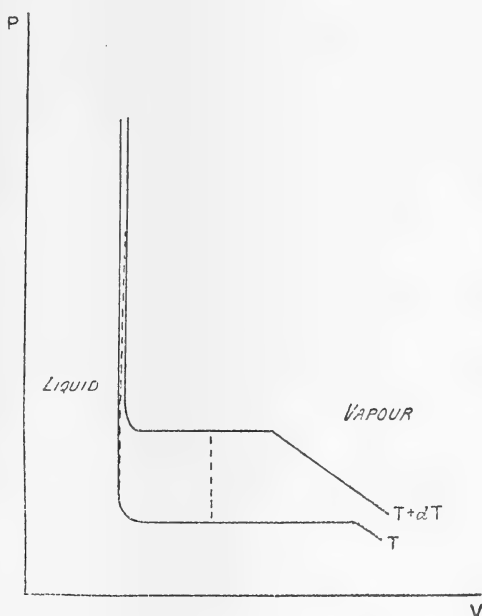
The quantities occurring in this expression are known at least approximately for a number of liquids. In the following table are given the results obtained from data taken principally from Landolt & Börnstein's *Tabellen*, Castell-Evans' Tables, and Winkelmann's *Handbuch*.

Before giving the actual examples, however, it may be well to point out that the introduction of Dupré's idea, in its original as well as in its modified form, viz. that the internal pressure of a liquid may be measured by the latent heat of vaporization *per unit volume of liquid*, apparently leads to an expression which is in disagreement with the well-known Clapeyron expression

$$T \frac{\partial p}{\partial T} = \frac{L}{v_2 - v_1},$$

\* It will be observed that this result, although deduced on the assumption that  $K$  varies with temperature and is connected with  $l$  by the relation  $K - l = T \frac{\partial K}{\partial T}$ , does not prove the validity of the latter relation. Thus if we assumed that  $K$  is independent of temperature and therefore  $\frac{\partial K}{\partial T} = 0$ , we should still obtain the same final result, viz.  $l = T \frac{\partial p}{\partial T}$ .

for in this case we are equating the expression  $T \frac{\partial p}{\partial T}$  to the latent heat of vaporization per unit volume of vapour (approximately), while in the former case the latent heat referred to unit volume of liquid. The distinction really hinges on the fact that the system to which we have applied van der Waals' equation is the liquid one alone, and the expression  $\frac{\partial p}{\partial T}$  refers to the liquid state. That this may be a magnitude of quite a different order from the corresponding term for the saturated vapour is seen by a glance at the *p.v.* diagram for the liquid vapour system in which the dotted lines indicate the quantities referred to\*.



In the following table the Trouton constant for the substances examined is also included, as there appears to be a close connexion between the two expressions as regards their range of applicability.

\* The connexion between  $\left(\frac{\partial p_{\text{liquid}}}{\partial T}\right)_v$  and  $\left(\frac{\partial p_{\text{vapour}}}{\partial T}\right)_v$  is

$$\left(\frac{\partial p_{\text{liquid}}}{\partial T}\right)_v = \left(\frac{\partial p_{\text{vapour}}}{\partial T}\right)_v \cdot \frac{v_{\text{vapour}}}{v_{\text{liquid}}}$$

Substance.	Temperature to which the expression $-\frac{T\alpha_1}{\rho\beta}$ refers.	Temperature to which $L$ refers.	$-\frac{T}{\rho} \frac{\alpha_1}{\beta}$ .	Observed.	Trouton Constant.
Ethylene chloride .....	0° C.	0° C.	89.3 cal.	85.4 cal.	23
Ethyl chloride .....	0	21	109	100.1	21.18
Ethyl bromide .....	0	38	65.5	61.65	21.52
Ethyl iodide .....	0	71.3	52	46.87	21.18
Methyl acetate .....	0	0	94.7	113.89	25
Ethyl acetate .....	0	(75.9)	86.9	{ 86.7	20.88
Benzene .....	15	{ 0	98	{ 102.14	20.8
Toluene .....	0	15	98	86.67	20.8
Xylene .....	0	110.8	98.3	83.55	20.02
Cymene .....	0	139	95.7	78.25	20.15
Bromine .....	0	175	90.1	66.3	19.83
Mercury .....	0	58	37.3	45.6	21.78
Acetone .....	20	0	24.68	71.12 at 0°	21.5
Carbon disulphide .....	0	0	130.3	139	22.84
Ether .....	0	0	70.4	89.5	20.84
Chloroform .....	0	0	91.2	{ 93.5	21.94
Carbon tetrachloride .....	0	0	57.6	{ 94	21.74
			48.6	67	20.62
				52	
Methyl alcohol .....	0	0	123.6	290	24.67
Ethyl alcohol .....	0	0	117	221-229	26.39
n. Propyl alcohol .....	0	0	68.7	165.9	26.59
Isopropyl alcohol .....	0	82	89	161	26.46
n. Butyl alcohol .....	0	116	79.2	143	26.16
Water .....	0	...	negative quantity	{ 600	25.90
	4°	...	zero	{ (circa)	
	> 4°	...	positive quantity		
Acetic acid .....	0°	118°	163	{ 84.9	13.74
				{ 92.7	



It is evident that a comparison between observed\* and calculated values should only be carried out at the same temperature. Owing to lack of data, however, it has been necessary in several cases simply to quote such results as are available. When the difference between the temperature in the two cases is great (*e. g.* xylene, cymene, acetic acid, &c.), one cannot expect the results to be very comparable, for latent heat has in general a fairly high (negative) temperature coefficient. A more important point still, however, has reference to the compressibility data. An accurate determination of the compressibility of a liquid involves very great experimental difficulty, and it is therefore to be expected that the results for the substances quoted may in some cases be subject to rather large error (*cf.* Quincke, *Annalen der Physik*, xlv. p. 776 (1891)). Further, since for all the substances mentioned with the exception of mercury, the compressibility alters, *i. e.* decreases, as the pressure increases, to obtain comparable results the values should be extrapolated to zero pressure. This has only been done in a few cases (*cf.* Ritzel, *Zeitsch. physik. Chem.* lx. p. 319 (1907)).

The determination of the latent heat of vaporization itself may also involve considerable error†. With these reservations one is justified in considering that the relation holds for liquids which are not associated either in the liquid or vapour state. For these same substances one obtains the "normal" value for the Trouton constant. On the other hand, in the case of those liquids such as the alcohols which are known to be considerably associated in the liquid state into di- and tri-molecules, but are practically non-associated in the state of vapour, it will be observed that the calculated latent heat is only about one half of the observed. For these substances the Trouton constant is abnormally high. In the case of water, owing to the existence of the density maximum

\* In several cases the "observed" value is really calculated from the Clapeyron equation.

† In this connexion Nernst ('Applications of Thermodynamics to Chemistry,' p. 103) employs the relation

$$\lambda = R \frac{T_1 T_2}{T_1 - T_2} \left(1 - \frac{p}{\pi}\right) \log \frac{p_1}{p_2},$$

in which  $p_1$  and  $p_2$  denote the vapour pressures corresponding to  $T_1$  and  $T_2$ , two temperatures which differ by so small an amount that their geometric and arithmetic means may for practical purposes be set equal to one another. This mean temperature is the one to which  $\lambda$  refers," . . . "in general the heats of vaporization calculated with its aid are more accurate than those determined calorimetrically."

at  $4^{\circ}$  C. (under ordinary pressure), the coefficient of expansion is negative from  $0^{\circ}$  C. to  $4^{\circ}$  C. and thereafter positive, thus causing a corresponding change of sign in the calculated value of the latent heat. In the special case of acetic acid, the calculated latent heat comes out approximately double the observed. The Trouton constant is abnormally low. This behaviour is due to the fact that not only is the liquid associated but the vapour is also polymerized considerably and apparently to a higher *degree* of polymerization. Ramsay and Young\*, employing the Clapeyron equation, found that the latent heat of vaporization of this substance *rose* with rising temperature, reaching a maximum at about  $110^{\circ}$  C. ( $L=92.79$  cal.), thereafter steadily decreasing.

In the case of associated liquids it is generally assumed that the observed latent heat of vaporization consists of two parts—one part being the heat required to isothermally cause the breaking down of the complex molecules into the simple form, and the second the heat required for the molecular spatial distribution change which is involved in vaporization. Since the “calculated” values of this paper do not take any direct account of heat required to cause association to disappear, one would expect the calculated values to be less than the observed. Such is the case; and if we assume that the discrepancies observed may be given a quantitative significance, it would appear that it requires approximately the same amount of heat to cause the depolymerization of the molecules as it does to vaporize the resulting simple molecules. To account for the behaviour of acetic acid we must assume that the “latent heat of depolymerization

\* Journ. Chem. Soc. xlix. p. 790 (1886).

In the case of methyl alcohol—whose factor of association in the liquid state at  $20^{\circ}$  C. is as large as 2.32,—Ramsay and Young found that at this temperature the density of the saturated vapour was 16.23, indicating a molecular weight of 32.46. The theoretical molecular weight is 32. On the other hand, in the case of acetic acid,—whose factor of association in the liquid state at  $20^{\circ}$  C. is 2.13,—Ramsay and Young found that the vapour density was 59.3, indicating a molecular weight of 118.6 while the theoretical is 60. This is sufficient to indicate the extraordinary behaviour of the vapour, though the figures appear to indicate that the degree of association in the vapour is not quite so large as in the liquid. In this connexion, however, attention should be drawn to the observation made by Ramsay and Young, viz. “Condensation takes place before the pressure becomes nearly constant; when a considerable amount of liquid is present, however, pressure remains nearly constant with decrease of volume.” The acid acts in fact as though it consisted of more than one substance. Further, Ramsay and Young remark that in consequence of this abnormal behaviour “the numbers [for the density of the vapour] must be regarded as *minimum values*, although above  $40^{\circ}$  it is probable they are nearly correct.”

of the liquid" minus the latent heat of polymerization of the vapour is a negative quantity, *i. e.* heat is evolved in this part of the process. Now as the temperature rises the degree of association in the liquid and vapour states will decrease but not necessarily at the same rate. It is probable that the vapour depolymerizes much more quickly than the liquid. There must therefore be a temperature at which there is equal polymerization in both the liquid and vapour phases.

At this temperature therefore the expression  $T \frac{\alpha_1}{\beta}$  should hold good. This cannot be tested owing to the want of the necessary data.

The points which have been discussed above have considerable bearing upon the Trouton constant itself. Thus, it

would seem that if one wishes to make the expression  $\frac{ML}{T}$

really comparable for all substances, it should be made independent of the heat required to cause depolymerization of the molecules. One might perhaps accomplish this by

employing the expression  $\frac{T}{\rho} \frac{\alpha_1}{\beta}$  instead of  $L$ , and write the

Trouton constant in the form

$$\frac{M\alpha_1}{\rho\beta} = \text{const.},$$

where  $M$  is the theoretical molecular weight and the other quantities hold for the boiling-point of the liquid. In this case, for normal substances the Trouton constant has its usual value. For the alcohols, however, the value is only about 13, and for acetic acid it is about 26. The constant is therefore not any more general in its character than before; and it is doubtful if the above changes possess any advantage over the usual method of stating this semi-empiric law. It should be pointed out also that the actual values one obtains for the compressibility or expansion of a polymerized liquid must depend to a certain extent on the actual polymerization existent in the liquid; for it has been established that there is definite equilibrium between simple and polymerized molecules in the liquid state, this equilibrium being shifted by external changes, such as temperature or pressure, in accordance with the principle of Le Chatelier. Thus on increasing the pressure the system will change in the direction corresponding to decrease in volume, so that the observed change of compressibility of a polymerized liquid

with pressure depends on two factors, (1) the actual alteration in the spatial distribution of the molecules, and (2) the change in the degree of polymerization. If this second factor is not negligible compared to the first, it would no longer be justifiable to consider the expression  $-\frac{T\alpha_1}{\rho\beta}$  as referring to that part of the latent heat of vaporization which takes account only of the transfer of the *simple* molecules from the liquid to the vapour state; and hence the conclusion that the heat required for the depolymerizing process is approximately one half of the total, would no longer be valid. Evidence—of a qualitative nature—in favour of the former conclusion, however, is furnished by the fact that the change of compressibility with pressure, especially at low pressures, gives much the same type of curve for normal and abnormal liquids alike. At the same time the quite anomalous results obtained with water have so far prevented any satisfactory generalization being made.

The results of the foregoing considerations may perhaps be summed up as follows.

The latent heat of vaporization  $L$  of a liquid per gram is connected with the compressibility  $\beta$  and the coefficient of expansion  $\alpha_1$  of the liquid by means of the relation

$$L = -\frac{T}{\rho} \frac{\alpha_1}{\beta}.$$

The applicability of this relation appears, however, to be restricted to normal liquids alone.

## XXIX. *Delta Rays*. By NORMAN CAMPBELL \*.

- 1-3. Nature of the problem.
- 4-7. Experimental arrangements.
- 8-10. Incidence and emergence radiations.
- 11, 12. Influence of the speed of the primary rays.
- 13. Influence of the emitting substance.
- 14-16. The effect of reflexion.
- 17, 18. The real delta rays.

Summary.

Appendix on high resistances for electrostatic measurements.

1. **I**T is now generally recognized that the slow moving electrons emitted by a plate covered with a substance emitting  $\alpha$  rays, called by J. J. Thomson delta rays, represent, at least in part, a secondary radiation excited by the alpha rays in any solid body on which they fall. Numerous experiments

\* Communicated by the Author.

on radiation of different types have shown that in general the secondary radiation emitted by a body is in no way dependent on its physical condition, or on the relation between the atoms of which the body is composed; it depends solely on the nature of those atoms. Accordingly, analogy would suggest that delta rays must be emitted also by gases under the influence of alpha rays. It is apparently admitted\* that the process which appears as the emission of delta rays when alpha rays fall on a solid is the same as that which appears as ionization when the alpha rays pass through a gas. The experimental difference between the two phenomena arises from the facts that, in the case of the gas, the electrons are emitted throughout a finite volume and not only at a surface, that the electrons liberated combine with neutral atoms to form ions, and that the positively charged remainders of the atoms from which the electrons are emitted can move under the action of an electric field. It was therefore suggested to me by Prof. Bragg that the study of the delta rays has been neglected unduly, and that the further investigation of them might throw light upon the extremely important problem of the mechanism of ionization. The work that has been done hitherto† has been confined to a few measurements of the speed of the electrons in special cases; it appears desirable to inquire by what circumstances that speed and also the number of the electrons emitted are determined.

2. In order to make a complete determination of the velocity of the rays measurements must be made upon the effect of both an electric and a magnetic field upon their motion. Such measurements will give the value of both the velocity and the ratio  $e/m$ . However, since in the present investigation the value of  $e/m$  may be regarded as known, it is sufficient to study the action of the electric field only. The study of the action of a magnetic field according to the method of J. J. Thomson‡ yields definite results only when the rays are homogeneous, and is attended by the considerable experimental difficulty of obtaining a perfectly homogeneous magnetic field over a considerable area. Accordingly, a magnetic field was employed only when it was desired to prevent any of the rays leaving the surfaces from which they were emitted; no investigation of the effects of fields less than that required for this purpose has been made.

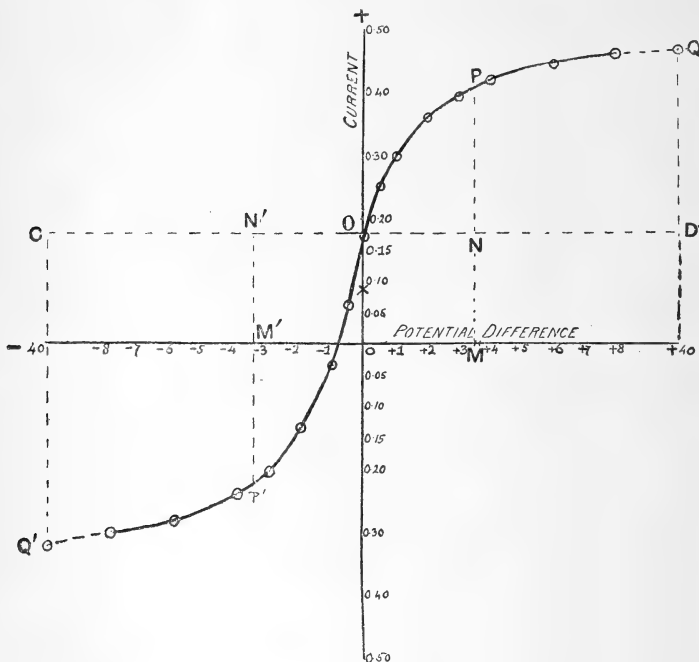
\* Cf. for example, Kleeman, Roy. Soc. Proc. A. lxxxiii. p. 195 (1910).

† J. J. Thomson, Proc. Camb. Phil. Soc. xiii. p. 49 (1904); E. Rutherford, Phil. Mag. x. p. 193 (1905); Ewers, *Phys. Zeit.* vii. p. 148 (1906); Logeman, Roy. Soc. Proc. A. lxxviii. p. 212 (1906).

‡ J. J. Thomson, 'Conduction of Electricity through Gases,' p. 67.

3. The principles involved in the use of the electric field are extremely simple. Let two bodies A and B be emitting the rays, and let the circumstances be such that all of the rays emitted by one body strike the other, when the bodies are at the same potential. Let the current received by A be measured when B is at different potentials,  $V$ , the potential of A being always 0. Let this current, when  $V$  is 0, be represented by  $O$ : it will be made up of two parts, (1) a part independent of  $V$ , due to the charge carried by the alpha rays themselves and similar causes, and (2) the difference between the number of rays emitted by A and those emitted from B and received by A. When  $V$  is positive, the number of rays

Fig. 1.



emitted by A will be unchanged, while the number of rays received by A from B will be decreased by the number of rays emitted from B which have a speed less than that corresponding to  $V$ . Accordingly  $PN$ , which is the difference between the current for  $V=0$  and that for  $V=ON$ , represents the number of rays emitted from B which have a speed

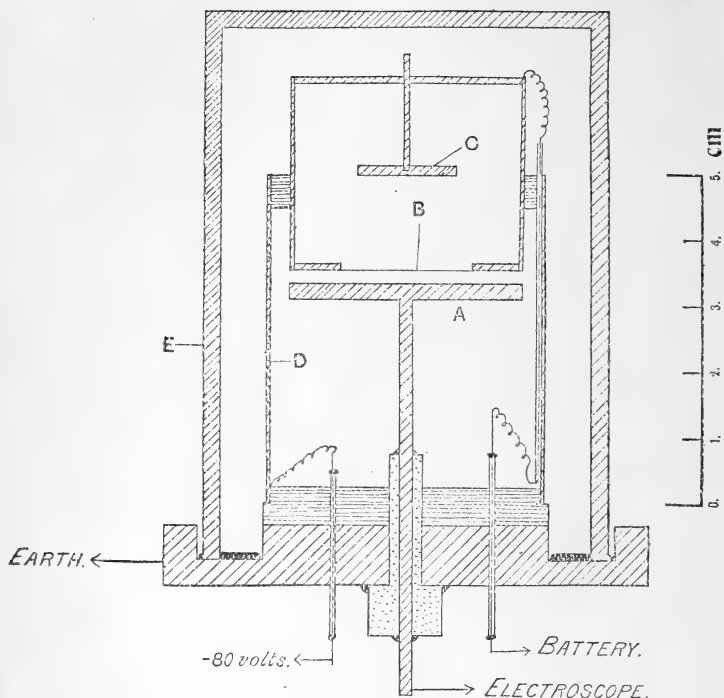
less than that corresponding to ON. In the same way, if  $V$  is negative,  $P'N'$  will represent the number of rays emitted by A which have a speed less than that corresponding to ON'. The curve will be divided into two parts by the line CD, the upper half representing the properties of the rays emitted from B and the lower half those of the rays emitted by A.

It is important to notice that this simple relation holds only if the condition is fulfilled that, in the absence of the field, all the rays emitted by one plate fall on the other. For, if, when no field is acting, some of the rays emitted by A can strike A or some third body not electrically connected to B, a positive potential on B will change the current, not only by diminishing the number of rays emitted by B which strike A, but also by increasing the number of rays emitted by A which strike B. The necessary condition is not very easy to realize experimentally, but preliminary observations showed, as might be expected, that the form of the curves obtained varied considerably with small differences in the arrangement of the apparatus unless it was fulfilled. Indeed, at first sight it might appear that it is geometrically impossible to fulfil the condition. For, on the one hand it is clear that the emitting surfaces must be plane, or the rays from one body might strike the same body again; and, on the other hand, that each body must surround the other completely, lest the rays emitted strike some third body. However, if the active surface itself is not employed as one of the bodies, the conditions can be fulfilled. Fig. 2 (p. 208) shows the form of apparatus finally adopted for the first part of the investigation. The drawing is approximately correct in scale.

4. A and B are the bodies from which the delta rays are emitted. A is a solid plate connected to the apparatus for measuring the current by a rod passing through the brass base plate and insulated by an amberoid stopper. B is a brass cylinder; in the end facing A is a circular hole which is covered with a layer of some material thin enough to transmit alpha rays. The polonium plate C is placed at such a distance above this end of B that all the rays which pass through the hole (and are not scattered considerably) fall upon A. Accordingly delta rays can only affect the measurements if they are emitted from either A or B. To prevent these delta rays striking the cylinder D which surrounds A and B, D is maintained at a potential of  $-80$  volts. It is insulated from the base plate by the ebonite plate, the surface of which is covered almost completely

with aluminium foil connected to the base plate electrically. B can be maintained at any desired potential by a battery of

Fig. 2.



cells in combination with a potentiometer subdividing one of them. For the purpose of this paper the E.M.F. of a lead accumulator has been taken as 2 volts.

The brass cover E, cemented to the base plate with a wax composed of rosin and beeswax, enclosed the entire apparatus. A high vacuum was established first with a Gaede pump and then with charcoal and liquid air, which was connected to the vessel throughout the observations by a tube not shown in the drawing. As previous observers have noted, the extreme vacuum obtainable by this method was not absolutely necessary, but the use of the charcoal rendered unnecessary any attention to very small leaks. A rise in the pressure of the gas in the vessel could always be detected by an increase in the current that passed between the electrodes when a magnetic field was applied to prevent the emission of delta rays.



This apparatus appears to represent as near an approach as can be made to the requisite condition. Any divergencies from it will be noted in the discussion of the results. If the active plate itself were used in place of the layer covering the hole in the end of B, it would be impossible to prevent the alpha rays emitted obliquely from striking D and causing the emission of delta rays therefrom.

5. For the measurement of the current a compensation method is necessary, since the potential of the insulated electrode must not be allowed to diverge sensibly from zero during the observation, lest uncertainty be introduced as to the actual potential between the electrodes for which the current is being measured. With a sensitive electrometer measurements might be made by the ordinary method without allowing the potential of the electrode to change by more than 0.01 volt, but even such a small change is undesirable when small differences of potential between the electrodes are being investigated. The compensating current in these experiments was produced by applying a known potential by means of a potentiometer arrangement to one end of a high resistance, the other end of which was connected to the measuring instrument. The resistances employed are described in the Appendix. All measurements of current quoted in this paper are stated in terms of the potential in volts which it was necessary to apply to the resistance in order to compensate the current between the electrodes A and B.

It may be noted that there is some loss of sensitiveness involved in the use of the resistance arrangement rather than a saturated ionization current or a quartz piezo-electric for the production of the compensation current. For the difference of potential from earth which will be ultimately attained as the result of a given residual current is proportional to the resistance between the electrode and earth. In the case of the liquid resistance this resistance is several thousand times less than it would be if either of the other arrangements were used. But it must be remembered (1) that the unsaturated flow of electricity between the electrodes in itself acts like a resistance to earth\*, and (2) that the time for which the current can be allowed to flow, before it is decided whether compensation is complete, is limited by the time during which the zero of the indicating instrument will remain constant. With the arrangement used not more than one half of the sensitiveness that might have been attained

\* Cf. Campbell, Proc. Camb. Phil. Soc. xv. p. 134 (1909).

was sacrificed, and it was clear throughout that the uncertainty due to errors of compensation were considerably smaller than errors due to other circumstances over which no control could be attained.

6. As an indicating instrument a sensitive Wilson tilted electroscope was used. Some experiments were tried with an electrometer with a sensitiveness of 5000 divisions for a volt, but no more accurate results could be attained. The extremely short period of the electroscope gives it a great advantage over the electrometer when it is desired to discover, by earthing the electrode, whether there has been any deviation of the potential from that of earth. When the electric field between the electrodes was so great that the current was saturated, the potential which had to be applied to the resistance to attain compensation could be determined with complete certainty to within 0.003 volt.

7. Experiments were first made to discover whether there was any change of the velocity of the delta rays with a change in the velocity of the exciting alpha rays. For this purpose the form of the relation between potential difference and current was investigated when the hole in B was covered with aluminium leaf of different thicknesses. A was covered with an aluminium plate throughout. The thinnest leaf used was equivalent in surface density to about 1 mm. of air; the thickest through which the rays could be measured was equivalent to about 4.1 cm. Using Rutherford's measurements on the velocity of alpha rays, it appears that in the first case the rays emerging from B and striking A must have had a mean velocity of about  $2.0 \times 10^9$ ; in the latter case of about  $1.5 \times 10^9$ . It must be remembered that the potential required to stop the rays is proportional to the square of their speed, so that, if the velocity of the fastest delta rays had varied in the same ratio as that of the fastest alpha rays, the potential required to stop them would be nearly twice as great with the thinnest foil as with the thickest. Of course the alpha rays were not homogeneous in speed, since some of them passed obliquely through the aluminium leaf, but it is obvious from the values of the total current that the superposition of thicker absorbing layers must have produced a considerable change in the average velocity of the rays.

8. The results of the measurements are recorded in Table I. The columns marked 1-9 give the observations made when the hole in B was covered with layers of aluminium of which the surface density (grm./cm.<sup>2</sup>) is given in the first row. The second row gives the current when the difference of potential between A and B was zero; the third row the value

TABLE I.—Aluminium.

	1. +   -	2. +   -	3. +   -	4. +   -	5. +   -	6. +   -	7. +   -	8. +   -	9. +   -	Mean. +   -
Thickness of Al...	$0.11 \times 10^{-3}$	$0.22 \times 10^{-3}$	$1.40 \times 10^{-3}$	$2.69 \times 10^{-3}$	$3.98 \times 10^{-3}$	$4.55 \times 10^{-3}$	$4.77 \times 10^{-3}$	$4.99 \times 10^{-3}$	$5.20 \times 10^{-3}$	
V=0 .....	+0.134	+0.156	+0.231	+0.239	+0.211	+0.175	+0.152	+0.115	+0.45	
V=0 (magnet) ...	+0.10	+0.120	+0.125	+0.123	+0.114	+0.089	+0.083	+0.063	+0.45	
V=40.....	0.443 0.445	0.353 0.480	0.373 0.576	0.375 0.637	0.357 0.590	0.293 0.499	0.216 0.394	0.190 0.320	0.079 0.090	
V= $\frac{1}{2}$ .....	.305 .227	.258 .250	.270 .212	.254 .209	.246 .217	.266 .233	.259 .205	.210 .200	.320 .234	0.258 0.219
1 .....	.435 .396	.389 .435	.425 .412	.403 .413	.389 .399	.392 .417	.415 .401	.415 .416	.520 .357	.408 .412
2 .....	.678 .623	.600 .630	.640 .650	.617 .655	.610 .635	.630 .619	.641 .620	.695 .656	.659 .600	.626 .636
3 .....	.766 .758	.715 .765	.753 .769	.730 .772	.733 .750	.740 .759	.790 .765	.729 .763	.696 .769	.744 .763
4 .....	.856 .832	.820 .830	.862 .840	.803 .844	.820 .839	.841 .830	.890 .837	.842 .845	...	.842 .837
6 .....	.923 .906	.899 .921	.930 .930	.890 .925	.915 .910	.922 .920	.962 .949	.915 .938	...	.919 .925
8 .....	.958 .964	.946 .965	.933 .965	.942 .970	.935 .940	.983 .950	1.010 .975	1.000 .985	...	.963 .964
40 .....	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	1.000 1.000	...	1.000 1.000
Ratio +/- .....	1.00	0.74	0.65	0.59	0.61	0.59	0.55	0.59	0.88?	
Ratio $\delta/\alpha$ .....	7.9	10.4	11.2	12.4	12.8	16.4	14.4	26.8	33.8?	

of the current for the same difference of potential when the apparatus was introduced into a magnetic field so strong that a further increase in it produced no change in the current. The next nine rows give the form of the curve, exemplified by fig. 1, which is plotted from column 6. The fourth row gives the absolute value of the maximum ordinate QD or Q'C, the former being placed in the column marked +, the latter in the column marked —. The eight rows immediately below the double horizontal line give the values of the ordinates PN or P'N' corresponding to values of V denoted in the first column; those in the column marked + denote the values when B is positive to A, those in the column marked — those when B is negative to A. In order to enable a comparison to be made between different columns the values are not expressed in absolute measure, but as fractions of the maximum ordinate. The absolute value in any case can be found by multiplying the number recorded by the number in the same column immediately above the thick line. The last two rows will be referred to later.

9. According to § 3 the columns marked + refer to the properties of the rays emitted by B, those marked — refer to the properties of the rays emitted by A. In accordance with the nomenclature introduced by Prof. Bragg, we may call these rays respectively “emergence” and “incidence” radiation. The first point which needs inquiry is the relation between the incidence and emergence radiations. It will be noted that the amount of the emergence radiation, given by the fourth row (+ column), is never greater than the amount of the incidence radiation (— column); when the layer through which the rays emerge is very thin the emergent and incident radiations appear to be equal, while, as that layer increases in thickness, the emergent radiation decreases relatively to the incident. The ratios of the emergent to the incident radiation are given in the tenth row; it will be seen that this ratio appears to be constant after a certain thickness of the layer is reached. Columns 7 and 9 are somewhat anomalous, but there are other indications that column 7 is affected by some source of error, while the current dealt with in column 9 is so small that the apparently large divergence of the ratio is not really greater than the possible error of observation.

This result is certainly surprising and difficult to explain. Further investigation of the point is certainly necessary. But it may be noted that in all the experiments described in this paper, and in a large number of preliminary observations with different apparatus, of which the results are not

recorded, the same feature has been noted. Cases are observed in which the emergence radiation is nearly equal to the incidence, but none in which it is certainly larger. The exact contrary is, of course, true of all other forms of radiation.

10. The quality of the emergence and incidence radiations next requires attention. If the quality of both is the same, the numbers in the columns marked + should be the same as those in the corresponding columns marked —. It will be seen that there are considerable divergencies between the + and — columns, and that these divergencies are certainly greater than can be accounted for by mere errors of observation; the observations were sufficiently accurate to leave no uncertainty about the second figure, except in the case of column 9. But it will be seen also that the sign of the difference between the + and — columns is not constant in different series, and that in the last column marked “mean,” which gives the arithmetic mean of the corresponding numbers for columns 1–8, the divergence has practically disappeared except for the value  $V = \frac{1}{2}$ . The divergencies are easily explained without assuming any difference in quality between the emergence and incidence radiation.

It is obvious that the form of the two branches of the curve of fig. 1 will be modified considerably if any point other than  $O'$  is taken as the zero from which all measurements are made.  $O'$  has been actually taken as the point corresponding to the condition that no difference of potential is imposed externally on A and B. But it does not follow that this condition represents the state in which A and B are actually at the same potential, still less the state in which there is no resultant electric field in the space between them. In the first place, there may be small thermoelectric differences of potential in the circuit connecting A and B, and, in the second place, it must be remembered that the surrounding cylinder D has a potential widely different from that of A and B. If A and B are not perfectly symmetrically situated with respect to D, there will be a resultant electric field tending to drive the rays to one plate rather than the other. As a matter of fact, it was found that the measurements for very small values of  $V$  were much less constant than those for large values, when these sources of error would be less important. The same value could not always be recovered during the same series of observations, and the value varied considerably between different series separated by an interval in which the apparatus had been taken down. In all cases, a much better agreement between the values for

the emergence and incidence radiation could be obtained by taking a value for  $V=0$ , which was not certainly less correct than that given by the mean of the actual measurements. On these grounds I am inclined to conclude that there is no difference of quality between the emergence and incidence radiation, and that the small apparent differences are accidental and due to experimental uncertainties.

11. If this conclusion be accepted, the second part of the investigation, the comparison of the quality of the delta rays for different velocities of the alpha rays, is rendered easier. For, if the two branches of the curve are really similar, we may avoid placing great reliance upon measurements at the zero by simply adding the ordinates  $PN$  and  $P'N'$  (fig. 1) corresponding to the same difference of potential with a different sign. The results of such addition are given in Table II. Here again the columns 1-9 represent the results of different thicknesses of the layer covering  $B$ , and hence, for different velocities of the emergent alpha rays. The numbers in any column represent the ratio of the arithmetical sum of the currents obtained for positive and negative values of  $V$  given in the first column to the sum of those values for  $V=40$ . (It appeared throughout that no change in the current occurred on increasing the value of  $V$  beyond 40 volts.) On the simple theory the numbers in any row should represent the fraction of the delta rays which have a speed less than that corresponding to the value of  $V$  in the first column.

It appears at once that the difference between different columns is very small. I am inclined to think that any apparent differences are due to the residual effect of the sources of error mentioned already: for, if there is an unavoidable difference of potential  $v$  between the electrodes, the measurements for an imposed difference of potential  $V$  will not represent the current due to  $V$ , but the sum of the currents due to  $V-v$  and  $V+v$ . If there is any difference, it is that the values of the current for high velocities of the alpha rays tend to be greater for small values of  $V$  and less for large values: that is to say, that there are more rays of very low and of very high speed, and fewer rays of intermediate speed. The experiments seem to establish conclusively that there is no very marked dependence of the velocity of the delta rays on that of the exciting primary rays: it is not certain that there is any dependence. Such a conclusion, if it is accepted, is obviously of the utmost importance for the theory of ionization by alpha rays. But

TABLE II.  
Aluminium.

[illegible]

before it can be definitely accepted a most important source of uncertainty which has been left unnoticed hitherto must be discussed; the discussion will be postponed till a few further facts have been recorded.

12. The third row of Table I, should represent the charge carried by the alpha rays themselves, and should, therefore, measure the number of alpha rays acting to produce delta rays. The numbers actually given require some correction, for, even in the absence of the polonium disk, the plate A tended to charge positively. Many blank experiments were made to determine this residual current, but the results obtained were not very consistent: the quantity which requires to be subtracted from the values in row 3 in order to obtain the true charge of the alpha rays is about 0.04, but the uncertainty is such that the resulting values cannot be relied upon in column 1 to 10 per cent., in column 9 to 100 per cent. This uncertainty, since it is the same for the whole curve, does not affect any of the other conclusions drawn. But the comparison of the total amount of alpha rays obtained in this way with the total amount of delta rays obtained by adding the corresponding + and - columns in row 4 lead to an interesting conclusion, the main features of which are not dubitable. In the last row of Table I, the ratio of the charge on the delta rays liberated to that on the exciting alpha rays is given: it must be remembered that the alpha rays carry a charge double that of the delta rays. It is clear that one alpha ray can liberate more than one delta ray, and that the number it can so liberate is of the order of 10. Apparently, then, the delta rays must come from a layer about 10 atoms thick. Further, it will be noted that the slower rays in general liberate more delta rays than the faster. This conclusion is in accordance with that derived from the study of ionization; indeed, it is the one conclusion attained in these experiments which might certainly have been anticipated.

Again, if the simple theory is correct, the difference between the values of " $V=0$ " and " $V=0$  (magnet)" should represent the excess of the number of delta rays tending to charge the plate A positively over those tending to charge it negatively; that is to say, it should be equal to the excess of the value in the fourth row marked - over that marked +. (In thinking out the signs it should be remembered that the - column represents the properties of the rays which are stopped by a negative potential on B and those, therefore, which tend to charge A positively.) The relation is not fulfilled, the difference between the numbers in row 4 being



generally greater than the difference between " $V=0$ " and " $V=0$  (magnet)," but there is a certain parallelism between the two differences: when one is large, so is the other. The general nature of the effect is such as would be expected; the discrepancy in magnitude will be noted in a subsequent discussion: it is in part due, no doubt, to the uncertainty about the true zero noted already. It may be noted that if a correction were introduced for the decay of the polonium the charge on the alpha rays would decrease continuously with an increase in the thickness of the absorbing layer.

13. Similar experiments, though less exhaustive, have been performed on copper, silver, and gold. In these cases A was covered by a plate of the metal impenetrable to alpha rays, while one thin leaf (in the case of silver also two leaves) were placed over B. The thickness (surface density) of the leaves was approximately as follows:—

Cu 0.0003 gr./cm.<sup>2</sup> : Ag 0.001 gr./cm.<sup>2</sup> : Au 0.0002 gr./cm.<sup>2</sup>

The results are given in Tables III., IV., V., which should be comprehensible without further explanation. A word

TABLE III.  
Gold.

	+	-	Sum.
$V=0$ .....	0.138		0.138
$V=0$ (magnet).	0.152		0.152
$V=40$ . ....	0.569	0.284	0.853
$V=\frac{1}{2}$ .....	0.216	0.199	0.208
1 .....	.362	.348	.355
2 .....	.533	.552	.543
3 .....	.663	.659	.662
4 .....	.735	.735	.736
6 .....	.805	.848	.827
8 .....	.893	.905	.900
12 .....	.966	.955	.962
40 .....	1.000	1.000	1.000

TABLE IV.  
Copper.

	+	-	Sum.
$V=0$ .....	0.123		0.123
$V=0$ (magnet).	0.135		0.135
$V=40$ .....	0.381	0.452	0.833
$V=\frac{1}{2}$ .....	0.266	0.266	0.266
1 .....	.420	.410	0.415
2 .....	.617	.608	0.613
3 .....	.748	.715	0.735
4 .....	.817	.812	0.814
6 .. .....	.898	.889	0.893
8 .....	.940	.934	0.936
40 .....	1.000	1.000	1.000

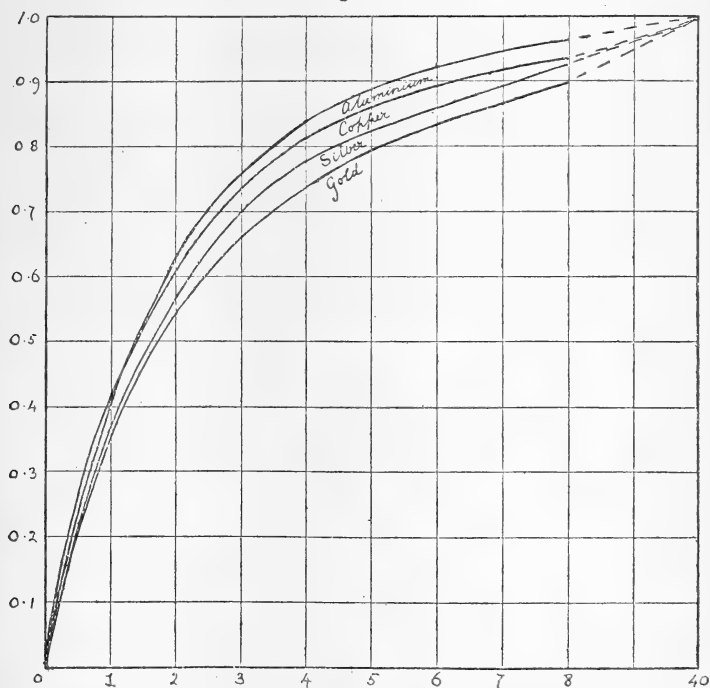
Ratio  $+/-$  0.84.



should be said about the columns marked "corrected" in Table V. It seemed clear in these observations that there was an error in the apparent zero. Accordingly, the results were corrected by taking as zero the point midway between the extreme values obtained for  $V = \pm 40$ . When this correction is made the values for one leaf and two leaves coincide very closely,

The results are of the same nature as those obtained with aluminium. There appears to be no difference in quality between the incidence and emergence radiations. For the thin layers of gold and silver the amounts of the two radiations appear to be equal, while for the thicker copper leaf the incidence is notably larger than the emergence radiation. It is of great interest to compare the quality of the radiations from the four metals used; for this purpose the "mean" curves of the sums of the positive and negative ordinates are plotted in fig. 3.

Fig. 3.



It will be observed that the rays from the silver and gold appear to be uniformly faster than those from the aluminium:

the copper appears to emit more slow rays, but also more fast rays than the aluminium. If then the curves can be taken as a measure of the speed of the delta rays, the very interesting conclusion appears indicated that the speed of the delta rays depends on the material from which they are emitted, and not on the velocities of the alpha rays exciting them. The delta rays would seem to be a true secondary radiation.

14. But before this conclusion can be accepted, the source of uncertainty must be discussed which has only been indicated hitherto. This source is the reflexion of the rays by the electrode, which was proved to exist for slow moving electrons by v. Baeyer\*. Do the curves given indicate anything about the velocity of the delta rays, or do they depend entirely upon varying amounts of reflexion at the electrodes?

There can be no doubt whatsoever from v. Baeyer's figures that reflexion will alter the form of the curves very materially. On this ground it is not pretended that the curves given can be taken as a measure of the proportion of rays of a given speed. But the measurements have all been performed under the same conditions, and conclusions have only been drawn from comparisons of different curves, not on comparisons of the same curve at different points. Are these comparisons rendered unjustifiable by the existence of reflexion?

It is not very easy to predict what would be the result of reflexion. In v. Baeyer's experiments the reflected rays were not subjected to an electric field, so that his results are not immediately applicable. Indeed he obtained intense reflexion when the rays were moving with a velocity corresponding to 40 volts, whereas the perfect saturation obtained in these experiments with that potential shows that the effects of reflexion are rendered negligible by the action of the field in retaining on the electrode any rays which strike it. For lower potentials the reflexion will have two effects. It will tend to decrease the number of rays moving up to an electrode against the electric field and retained by it; for some of them will be reflected and travel away with the field. On the other hand, it may cause some of the rays which have been emitted by the electrode to return to it after reflexion at the other electrode, even though the electric field tends to prevent the return. The first action will make the rays appear more easily stopped by an electric field than they

\* v. Baeyer, *Phys. Zeit.* x. p. 176 (1909), and earlier papers. Cf. also Ladenburg and Markau, *Phys. Zeit.* ix. p. 821 (1908).

would be if there were no reflexion: it will make the curve steeper than it should be. The second action will confuse the two branches of the curve, for they can be separated entirely only if on one branch all the rays from one electrode are received by the other even for the lowest potential differences. As the potential difference is increased the current will be changed, not only by the stoppage of rays leaving the electrode with which the branch is concerned, but also by the retention of more of the rays emitted by the other electrode. This action should make the rays appear less easily stopped by small potentials and make the curve flatter than it should be. I think, however, that there can be no doubt that the former effect, when the field and reflexion act in the same direction, is the more important.

Accordingly, though reflexion may modify considerably the form of the curve, there appears to be no reason why it should render invalid conclusions obtained by the comparison of different curves in all of which the geometrical arrangements and the material of the electrodes are the same, unless the average speed of the particles varies. In order to escape from the conclusion that the speed of the delta rays is independent of that of the alpha rays for the same metal by the consideration of reflexion, it must be supposed that the variation of reflexion with the speed is such as exactly to compensate the variation due to the direct effect of the change of speed. Such an assumption would appear somewhat forced, but it must be noted that the two effects act in compensating directions. von Baeyer shows that, within the range of speeds from 5 to 10 volts, with which we are largely concerned, reflexion increases with the speed. Now if, as we have concluded, reflexion tends on the whole to make the curve steeper, and the direct effect of an increase of speed undoubtedly tends to make the curve flatter, the two effects might compensate each other. But the closeness of the agreement shown in Table II., when considered in the light on the enormous reflexion found by v. Baeyer, appears to me to render such an explanation unsatisfactory.

It appears that reflexion might well be called in to explain the divergence between the estimates of the difference of the emergence and incidence radiation noted in § 12. For the existence of reflexion would doubtless tend to diminish the apparent inequality, as may be easily seen by a consideration of the analogous optical case. When  $V=0$  reflexion has a chance to exert its full effect; but when  $V=40$  and saturation is attained, reflexion has ceased to have any influence.

But the question of reflexion is most troublesome when

the curves with different metals are compared. If different metals have different reflecting powers, the various forms of curve might well be due to these differences, and not to differences in the speed of the rays. Now v. Baeyer has found it impossible to prove any clear difference between the reflecting powers of different polished metals, except possibly in the case of aluminium, which appears to reflect somewhat less than other metals. His results do not lead to the anticipation of such a difference as has been found between silver and gold, and the difference found between aluminium and gold is in the wrong direction. For it has appeared that reflexion should on the whole make the curve steeper: the curve for gold should on account of reflexion be steeper than that of aluminium. As a matter of fact it is flatter.

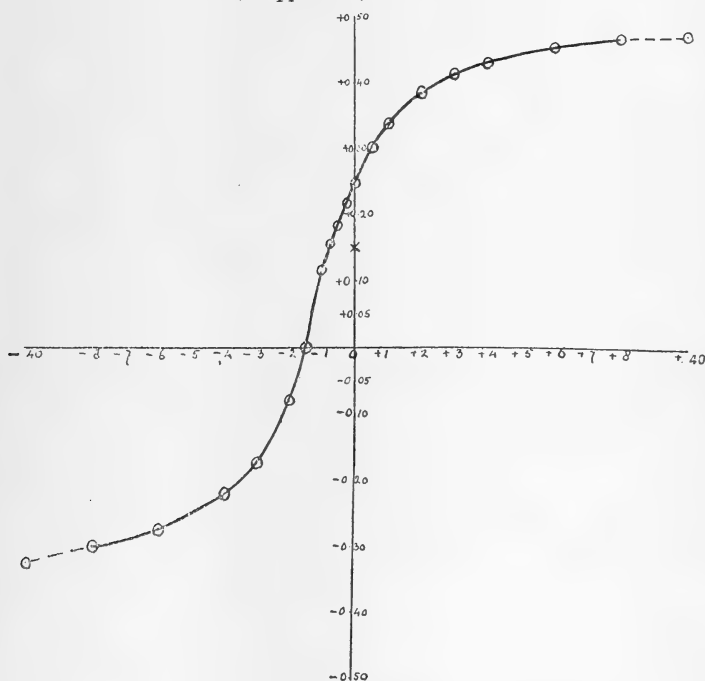
15. It appeared that useful information might be obtained on this important point if the curve were examined when one of the electrodes A and B was covered with one metal and the other with another. For if the curves previously obtained with different metals differed owing to a difference in the rays emitted from them, then if an electrode of copper were opposed to an electrode of aluminium, the part of the curve belonging to the aluminium electrode ought to show the quality of the aluminium rays and *vice versa*. But, if the curves differ owing to a difference in the reflecting power, then, since the aluminium rays are reflected at the copper, the part of the curve corresponding to the aluminium electrode ought to show the properties of the copper rays. The experiment is easily tried, but the results are rather difficult to interpret.

In order to explain the nature of the difficulty two of the curves obtained are plotted in figs. 4 and 5; they should be compared with the aluminium curve of fig. 1. It will be observed that in fig. 1 the change of curvature of the curve takes place at, or very near, the axis of zero potential difference: on the other hand, in figs. 4 and 5 the change of curvature is certainly not on that axis. In fig. 4 (where + refers to an aluminium electrode and - to a copper electrode) the change is certainly on the negative side of that axis; in fig. 5 (where + refers to a silver electrode and - to an aluminium electrode) the change is less obviously, but certainly, on the positive side. Similar results were observed for the combination gold-graphite, but the results are not included, for no success has been attained so far with graphite- or soot-covered electrodes; the difficulties are doubtless connected with an adhering film of air or moisture, which will be noted below.

16. The most obvious explanation of this difference is that when no difference of potential is imposed on the electrodes, there is still a difference between them owing to the Volta effect. Unfortunately the effect, though of the right magnitude (about 1 volt for Al-Cu and  $\frac{1}{2}$  volt for Al-Ag) is of the wrong sign; for this explanation would make both silver

Fig. 4.

A, Copper. B, Aluminium.

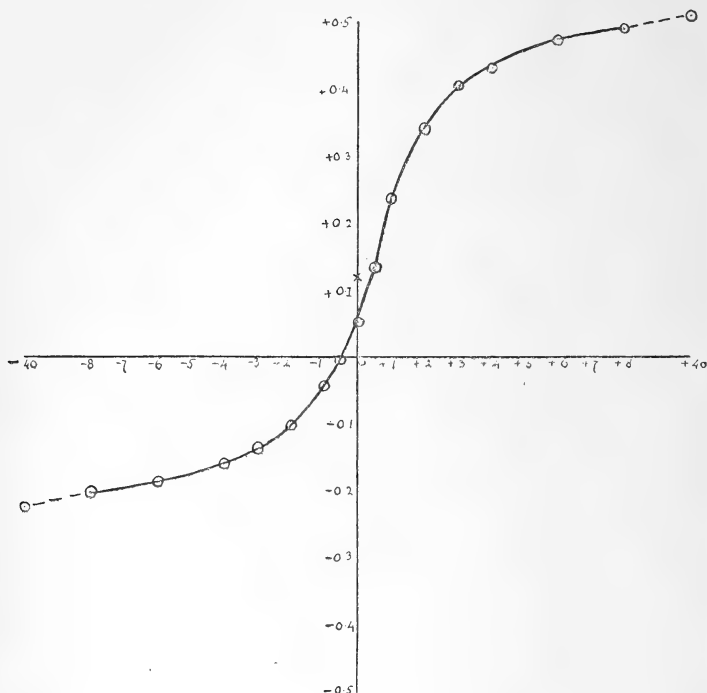


and copper positive to aluminium, whereas really the Volta difference of potential makes them negative. It seemed that a test of the correctness of the assumption might be made by finding the values of the total emergent and incident radiations, and comparing them with values found when both electrodes were of the same metal. If the values for the intrinsic difference of potential given above are correct (and no approximation nearer than  $\frac{1}{4}$  volt is attempted) we find, in the case of Ag-Al, 0.394 as the total emergence rays from silver and 0.353 as the total incidence rays for aluminium. Experiments made directly before and after these, when the electrodes were both of the same metal, gave 0.361 for the

emergence rays of silver and 0.480 for the incidence rays of aluminium. The agreement is not good. In the case of Cu-Al,

Fig. 5.

A, Aluminium. B, Silver.



the values for emergence aluminium rays and incidence copper rays were 0.362 and 0.445 respectively ; these are to be compared with 0.353 and 0.452. The agreement is much better. However, in neither case can the difference between the emergent and incident radiations found from the maximum values be reconciled by that found by comparing the values for  $V=0$  and  $V=0$  (magnet). (In figs. 1, 4, 5 the point corresponding to  $V=0$  (magnet) is marked by a  $\times$ .)

However, any other method of interpreting the curves which has suggested itself to me would appear artificial, and could lead to no convincing results. If, notwithstanding the discrepancies, the figures giving the qualities of the various rays are calculated as in Tables I., III., IV., V., the results given in Table VI. are obtained. In the case of the copper-aluminium



TABLE VI.

Copper-Aluminium.

Aluminium-Silver.

	Cu electrode.	Al electrode.	Al electrode.	Ag Electrode.
$V = \frac{1}{2} \dots$	0.272	0.193	0.224	0.259
1 .....	.430	.365	.374	.421
2 .....	.650	.600	.584	.633
3 .....	.751	.731	.705	.749
4 .....	.820	.823	.785	.815
6 .....	.888	.870	.878	.894
8 .....	.947	.949	.924	.946
40 .....	1.000	1.000	1.000	1.000

curve, it cannot be clearly decided which of the two branches resembles the aluminium curve more and which the copper; but in the case of the silver-aluminium curve it is clear that the branch corresponding to the silver electrode resembles more nearly the aluminium curve and *vice versa*. Hence, the only definite result which can be deduced on such assumptions is favourable to the hypothesis that the differences between the curves with different metals shown in fig. 3 are due to differences in reflexion and not to differences in emission, a conclusion contrary to that which has been attained in § 14. But the whole subject is so uncertain that it would be unwise to make any definite statement pending the further observations which are about to be undertaken.

17. Some experiments were made with the object of determining more closely whether the total radiation from different substances was the same, and whether there was anything of the nature of a true delta radiation from the polonium itself over and above the secondary radiation. The apparatus already described was not very well suited for the purpose, partly because it did not permit of the use of the bare polonium disk as one of the electrodes, partly because the use of the screen formed by the hole on B reduced unnecessarily the amount of the radiation, and partly because it was difficult to take the apparatus to pieces so as to introduce new substances without effecting small changes in the position of the parts. Accordingly, the disk A was replaced by the bare polonium disk, and D was replaced by a plain cylinder of the material under investigation, the top of which was parallel to and 2 mm. above the disk. With such an apparatus, the total saturated positive current should

measure the radiation from the polonium disk, the total saturated negative current the radiation from the other material; no simple interpretation can be put upon measurements of the current for differences of potential less than that required to give saturation. The charge due to the alpha rays themselves could not be determined, for a magnetic field would not stop the rays moving along the direction of the field: the effect of it would be to make the negative current appear rather too large and the positive rather too small.

It appeared at once that there was no very marked difference in the total negative current for different materials. But it was found impossible to determine within about 10 per cent. whether the current for all materials was the same. The reason for this impossibility lay in a progressive change in the current with the time, an effect which had been suspected before, but had not influenced measurements always expressed as fractions of the total current. After the vessel had been pumped out and the charcoal tube placed in liquid air, the current of both signs decreased at an approximately regular rate for at least 24 hours: the total change might amount to 10 per cent., but in no case was it certain that a steady condition had been obtained. There is no doubt that this change is due to the removal of films of air covering the electrodes; for if the pressure in the vessel were allowed to rise a few centimetres and then quickly reduced again, the leak was found to have risen again approximately to its original value. The following table gives the total positive and negative currents measured two hours after the application of liquid air: each figure is the mean of four observations which differ among themselves by not more than 10 per cent. The ratio of the positive to the negative current is much more constant, the extreme variation in the experiments on any one metal being 3 per cent.

TABLE VII.

	Al.	Cu.	Zn.	Sn.	Pb.	Paper.
+ current.....	8.58	8.56	8.57	8.29	8.64	8.86
- „ .....	6.56	5.85	6.73	6.12	6.63	6.61
Ratio +/- .....	1.32	1.46	1.27	1.35	1.30	1.34

18. It will be observed that the values of the ratio of the currents are the same for all metals except copper within the

limits of experimental error. The abnormal value for copper is doubtless due to the fact that the polonium is deposited on copper, and seems to suggest that there is still some unsuspected factor influencing the results. The saturating potential was taken at 120 volts, which gave values indistinguishable from those at 80 volts.

On the other hand, the current from the polonium itself is always greater than that from any other substance. This difference is not that between emergence and incidence radiations, for here the polonium is between the two metal electrode surfaces and both radiations are incidence\*. Experiments were tried in which the polonium was covered by a thin leaf of the metal forming the cylinder: the following are the results:—

TABLE VIII.

	Al.	Cu.
+ current.....	4.18	5.09
- „ .....	5.30	5.64
Ratio +/- .....	0.79	0.90

It would appear, then, that there is more delta radiation from the polonium than from any other substance, that is to say, there appear to be some true delta rays emitted from the polonium in the process of radioactivity, and not merely excited by the bombardment of the support by the alpha rays. Whether these rays are due to the bombardment of the polonium itself by the alpha rays which it emits, or whether they represent an entirely distinct form of radiation is probably a question of terminology.

## SUMMARY.

The following statement represents the main results which appear to have been attained in the investigation.

(1) There is no evidence that the speed of the delta rays is dependent on the speed of the alpha rays exciting them.

(2) There is no evidence of any difference in speed between the emergence and incidence radiations.

\* An experiment in which the polonium disk was supported from E and surrounded by a cylinder connected to the electroscope, showed that the result noted was not simply due to the fact that the disk was connected to the measuring apparatus.

(3) The incidence radiation appears never to be less than the emergence, though it is sometimes not greater. This conclusion conflicts with that obtained by Kleeman (*loc. cit.*) by an indirect method for gases. The difference is possibly due to the fact that in a gas the positively charged atoms from which the rays are emitted can move.

(4) It is doubtful whether the speed of the delta rays varies with the material from which they are emitted. Such a variation seems to have been detected, but considerations of the possible effect of the reflexion of the delta rays at the electrodes renders the *prima facie* evidence unreliable. It is worthy of note that the conclusion that the speed of the delta rays varied neither with the speed of the alpha rays nor with the material from which they are emitted, would be intensely interesting. In that case there would be apparently nothing left for them to vary with, and it would have to be concluded that the speed of the rays was a universal constant. Such a conclusion would not be inconsistent with the view put forward by Sir J. J. Thomson, that the ionization of a gas consists of the separation from the atoms of it of neutral bodies, similar for all atoms, which subsequently break into a positively and a negatively charged part. The view that there is an intermediate step between the impact of an alpha ray and the emission of an electron from the atom struck has also been put forward by Prof. Bragg.

(5) There is no evidence that the number of the delta rays emitted depends on the material from which they are emitted. The influence of adhering air-films makes small differences difficult to detect. It is possible, indeed, that no experiments have really been made on different materials, and that in all cases only the air-film has been dealt with. But the clear differences noted in § 13 between the observations with different metals seem to negative such a suggestion.

(6) There appear to be true delta rays emitted from the active substance emitting the alpha rays in excess of those due to the impact of those alpha rays on the support.

I should like to take this opportunity of expressing my great gratitude to Prof. Bragg and the University of Leeds, for their kindness in placing the resources of the physical laboratory at my disposal.

*Note added July 7.*

Experiments performed in the interval between writing the above paper and revising the proofs have altered materially the aspect of the subject. It appears now that the theory of

paragraph 3 is inadequate, and that the variation of the current between the electrodes with the potential difference between them is not determined primarily by the speed of the delta rays. Indeed it seems doubtful whether my own experiments or those of any other author in the same direction give any information, even as regards order of magnitude, as to the speed of these rays. The negative conclusions (1), (2), (4), (5), of the Summary are unaffected, but the evidence for (3) and (6) is completely destroyed. The account of the new experiments will be published as soon as possible: it has not been thought desirable to withdraw the present paper from publication, because, in order to arrive at the newer views, an account of the investigations already performed and the theory on which they are based is necessary.

#### APPENDIX.

The high resistances which have been used in these experiments for obtaining the compensating current appear to have uses for many physical experiments. Their properties have not been investigated exhaustively, only those important for the purpose in hand being tried. But the results obtained appear worthy of record. The resistances were originally prepared for quite different work\*.

The resistances consist of mixtures of xylol and absolute alcohol contained in glass tubes. The tubes are of thermometer bore 13 cm. long, and have bulbs blown at each end into which are sealed platinum wires. The glass round the wires is covered with sealing-wax for better insulation. The tubes are filled by suction and then sealed. They are held in an earthed metal clip which prevents conduction along the surface of the glass. The liquids used ranged from 1 part of alcohol to 8 of xylol to 1 part of alcohol to 3 of xylol; the resistances ranged from  $4 \times 10^{11}$  ohms to  $7 \times 10^9$  ohms. The resistance used in this work measured  $2.3 \times 10^{11}$  ohms. The materials used were the ordinary commercial articles dried by lime.

Bronson, in the paper describing the ionized air resistances usually known by his name, stated that he had tried liquid resistances, but had abandoned them owing to the difficulty of avoiding polarization effects. His choice of liquids must have been unfortunate, for the combination mentioned (which is almost the only one which has been tried) shows no such

\* Campbell, Proc. Camb. Phil. Soc. xv. p 322 (1909).

effects. If a large difference of potential (say 100 volts) is applied to the terminals and then reversed, the current does not attain a steady value for about a minute, but similar changes have often been noticed in ionization currents. The value of the steady current appears to be the same within 1 per cent. for either direction of the P.D. with any difference of potential between the terminals from 0.01 volt upwards. Moreover, the resistances showed no lag when rapidly changing potentials of the order of 0.1 volt were applied to the ends.

Within a range of 0.01 volt to 400 volts the resistances appear to obey Ohm's law perfectly within the experimental error. The temperature coefficient has not been investigated directly, but determinations of the conductivity made during three months, when the temperature of the laboratory must have varied  $5^{\circ}$ , agree within 1 per cent. No change of the resistance with the time after the first 24 hours of preparation has been noted.

It will be seen that these liquid resistances have many advantages over those of Bronson constructed with uranium or polonium. They appear able to be constructed with a resistance over a much wider range; the range mentioned could certainly have been extended widely below the lower limit. They are inexpensive and easy to construct, and they do not (like polonium resistances) change with the time. Moreover, the wide range over which Ohm's law is applicable is an immense advantage; it not only increases their usefulness for general purposes, but also renders their resistance extremely easy to determine. The resistance of a tube intended to be used for very low differences of potential can be measured by means of a high potential battery and a standardized galvanometer. Indeed, it appears that if such resistances were carefully standardized they would provide a far more convenient and much cheaper means of reducing electrostatic measurements of current to absolute units, than the standard capacities which are ordinarily used or quartz piezo-electric. They would probably not be quite so accurate, but for many purposes a loss of accuracy would be unimportant.

Leeds, April 1911.

XXX. *On Absorption and Dispersion* \*.

By ANDREW STEPHENSON †.

1. **W**HILE the ordinary theory of transmission through a medium is applicable only to the limiting cases of zero absorption and total reflexion, it has long been recognized that in transmitted light the dissipation of energy is not in general wholly due to scattering. It is evident that such dissipation is characteristic of a medium in the molecule of which the normal motions of the visible spectrum are subject to the influence of other normal motions of relatively small frequency.

Even with only a few slow modifying vibrations the spectrum may be of considerable complexity, since each element of freedom of higher frequency may contribute a large number of simple components in its free motion ‡. If now a train of frequency corresponding to any minor component is passing through the medium, it will generate a free oscillation in the coordinate to which the component is due, and since only a small part of the energy of the free oscillation belongs to the component, there must follow a dissipation of energy through emission. A steady state will result when the energy emitted by the coordinate in its free motion is equal to that gained from the incident train.

If the equation of motion of the coordinate affected is

$$z + \{\mu^2 + 2\alpha\mu n \cos(nt + \epsilon)\}z = 0,$$

where  $n/\mu$  is small, the amount of the absorption for the frequency  $(\mu \pm n)/2\pi$  is simply found when  $\alpha$  is small, not greater than 0.1 say.

The free motion is

$$z = \cos \mu t + \frac{1}{2}\alpha \{\cos(\overline{\mu - nt} - \epsilon) - \cos(\overline{\mu + nt} + \epsilon)\},$$

and the forced motion given by

$$\ddot{z} + \{\mu^2 + 2\alpha\mu n \cos(nt + \epsilon)\}z = c\mu^2 \sin \overline{\mu - nt} \quad . \quad . \quad (1)$$

is

$$z = -\frac{1}{4}\alpha c \mu t [\cos(\mu t + \epsilon) + \frac{1}{2}\alpha \{\cos \overline{\mu - nt} - \cos(\overline{\mu + nt} + 2\epsilon)\}] \\ - \frac{1}{2}c \frac{\mu}{n} \sin \overline{\mu - nt} \quad . \quad . \quad . \quad . \quad (2)$$

\* Cf. "On Displacement in the Spectrum due to Pressure," Phil. Mag. October 1910, p. 788.

† Communicated by the Author.

‡ "On the Forcing of Oscillations by Disturbances of Different Frequencies," § 3, Phil. Mag. July 1907, p. 115.

So that if the æther resistance is  $2\kappa\dot{z}$ , a free motion of amplitude  $\alpha c\mu/4\kappa$ , which is large compared with  $c$ , is maintained, and the rate of dissipation per molecule is proportional to  $\alpha^2 c^2/\kappa$ .

Hence the ratio of the absorption per unit length to the density is proportional to  $\alpha^2$ , that is, to the pressure: more briefly, the absorption per unit length is proportional to the square of the pressure. This simple quantitative relation holds good, it must be remembered, only when  $\alpha$  is small.

The absorption being inversely proportional to  $\kappa$ , which is very small, may be of considerable magnitude.

While radiation of frequency  $\mu/2\pi$  is almost altogether reflected, that of frequency  $(\mu \pm n)/2\pi$  is only slowly absorbed. By sufficient increase of pressure  $\alpha$  might be brought to such magnitude that both radiations would be transmitted with comparable absorptions. This condition would be the most favourable for the spectroscopic observation of the apparent group resonance.

2. If the solution (2) is carried to a higher order of approximation, we find that the amplitude of that part of the forced motion which has the same period and phase as the forcing disturbance is

$$\frac{(1 + \frac{3}{8}\alpha^2)c\mu^2}{(\mu - n)^2 - \mu^2}.$$

If therefore  $v$  is the velocity of transmission and  $V$  the velocity in free æther,

$$\frac{1}{v^2} = \frac{1}{V^2} \left\{ 1 + \frac{k\mu^2}{(\mu - n)^2 - \mu^2} (1 + \frac{3}{8}\alpha^2) \right\}.$$

Sellmeyer's formula for complete transmission thus undergoes modification when there is moderate absorption.

The velocity regarded as a function of the frequency exhibits a very rapid variation of small magnitude at the frequency  $(\mu - n)/2\pi$ ; there is therefore a definite limit to the accuracy of interpolation methods of determining the wave-length when there is absorption.

Only the frequencies which correspond to the simple normal oscillations, e. g.  $\mu/2\pi$ , give very large values for  $1/v$ , and that only when  $\alpha$  is small. As  $\alpha$  increases the velocities for  $\mu/2\pi$  and  $(\mu - n)/2\pi$  tend to become comparable. Evidently the true normal frequencies might be distinguished through their property of selective refraction at low pressure.

3. Since normal motions always interact and the necessary consequences are exhibited in the phenomena of radiating



and absorbing media, such interaction must be recognized as fundamental—just as the principle of the resonance of the simple system under isochronous force is fundamental in dealing with the more obvious phenomena.

*Note.*—In the paper on displacements in the spectrum due to pressure the suggestion as to the influence of radiation of frequency  $n/2\pi$  is over definite in giving the direction of the displacement. The effect of a slow oscillation, symmetrical or asymmetrical, may be in either direction in so far as general considerations of normal motions are concerned. The displacement must evidently be in the same direction as that under pressure.

March, 1911.

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XXXI. *Some Consequences of Fresnel's Reflexion of Light Theory, with Formulæ for Determining the Angle of Incidence in order to reflect 1/nth the Incident Light.* By ROBERT B. SANGSTER\*.

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THE greater part of this paper is taken up with the investigation of formulæ derived as consequences of Fresnel's Reflexion of Light Theory.

We have first, however, to deal with some trigonometrical relations connected with reflexion which are required later. The investigation is restricted to media which are homogeneous and isotropic, and as frequent reference will be made to the *first* and the *second* medium, either of which may be the denser, it is as well to state now that these terms indicate that the progress of the light is *from* the first *to* the second.

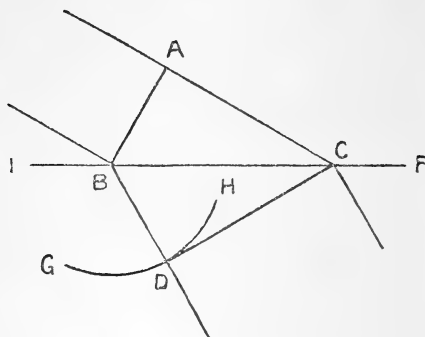
Let  $S$  (space) represent the volume generated in the first medium by a plane wave-front in unit time, and  $S'$  the volume generated in unit time in the second medium by the same plane wave-front, the transfer taking place at a plane interface. Also, let  $i$  be the angle of incidence,  $r$  the angle of refraction, and  $\mu$  the refractive index of the second medium with respect to the first. To remove possible ambiguity,  $\mu = V/V'$ , where  $V$  and  $V'$  are the velocities of light respectively in the first and second media.

Two obvious ratios of  $S$  to  $S'$  exist. At normal incidence  $S = \mu S'$  and at grazing incidence  $S/S' = 0$  or  $\infty$ . It may not be quite so obvious that at the incidence of maximum polarization  $S = S'$ . To show this, in fig. 1, suppose the plane of incidence to coincide with the plane of the paper,

\* Communicated by Dr. C. Chree, F.R.S.

and let AB represent the section of a plane wave-front incident on FI, the section through the plane interface bounding the second medium, in the figure supposed the denser. The edge B is just touching the interface. Through

Fig. 1.



A draw AC perpendicular to AB meeting FI in C. Let  $\mu = AC$ , then with centre B and radius  $BD=1$ , describe the arc HG. Through C draw CD touching the arc HG at D, and join BD. In the progress of the wave AB into the second medium, AC is the path of the extremity A, and the disturbance due to the extremity B reaches D in the time A reaches C; therefore, DC is a momentary position of the wave-front in the second medium, while

$$BD : AC :: 1 : \mu \quad . \quad . \quad . \quad (1)$$

Also, the areas ABC and BCD are generated in equal times, and we can assume unit measure for that dimension of these areas which is perpendicular to the paper, hence

$$\begin{aligned} S : S' :: \frac{\text{area}}{\text{ABC}} : \frac{\text{area}}{\text{BCD}} \\ :: BA \cdot AC : BD \cdot DC. \quad . \quad . \quad . \quad (2) \end{aligned}$$

But, the angle  $ABC = i = \tan^{-1} \mu$  (by hypothesis). Hence,  $\tan ABC = \mu/1 = AC/AB$ ; and  $BD=1$  when  $AC=\mu$ , (1); therefore,  $AB=BD$ . But AB and BD are sides of right-angled triangles standing on the same base BC, hence area  $ABC = \text{area } BCD$ , and  $S=S'$ .

We have now to find expressions for  $\sin i$  and  $\tan i$  when  $\chi S=S'$ , where  $\chi$  may be  $>$  or  $< 1$  but is always positive, and it may be stated here that this application and interpretation of  $\chi$  is adhered to throughout the paper.

When  $\chi S = S'$  (referring to fig. 1),

by (2),  $\chi \cdot BA \cdot AC = BD \cdot DC$ ,

by (1),  $\chi \mu \cdot BA = DC = \sqrt{(BA)^2 + \mu^2 - 1}$ ,

whence

$$BA = \sqrt{\frac{\mu^2 - 1}{\chi^2 \mu^2 - 1}}.$$

But,  $\tan i = \mu/BA$ ,

$$\text{wherefore } \tan i = \mu \sqrt{\frac{\chi^2 \mu^2 - 1}{\mu^2 - 1}} \quad \dots \quad (3)$$

Again,  $(BC)^2 = \mu^2 + (AB)^2$ ,

$$\text{therefore } BC = \sqrt{\frac{\chi^2 \mu^4 - 1}{\chi^2 \mu^2 - 1}}.$$

But,  $\sin i = AC/BC = \mu/BC$ ,

$$\text{wherefore } \sin i = \mu \sqrt{\frac{\chi^2 \mu^2 - 1}{\chi^2 \mu^4 - 1}} \quad \dots \quad (4)$$

Fresnel's formula for the ratio of reflected amplitude is  $\tan(i-r)/\tan(i+r)$  when the light vibrates in the plane of incidence, and  $\sin(i-r)/\sin(i+r)$  when the vibration is perpendicular to that plane, and we shall require these ratios expressed in terms of  $S$  and  $S'$ . Referring to fig. 1 where the angle  $ABC=i$ , and the angle  $BCD=r$ ,

$$\begin{aligned} \frac{\tan(i-r)}{\tan(i+r)} &= \frac{\sin i \cos i - \sin r \cos r}{\sin i \cos i + \sin r \cos r} \\ &= \frac{AC \cdot AB - BD \cdot DC}{AC \cdot AB + BD \cdot DC}. \end{aligned}$$

But, by (2),  $AC \cdot AB : BD \cdot DC :: S : S'$ , wherefore

$$\frac{\tan(i-r)}{\tan(i+r)} = \frac{S-S'}{S+S'} \quad \dots \quad (5)$$

$$\text{Again, } \frac{\sin(i-r)}{\sin(i+r)} = \frac{AC \cdot DC - AB \cdot BD}{AC \cdot DC + AB \cdot BD}.$$

But, by (1),  $AC = \mu$  when  $BD = 1$ , and therefore also

$$\mu \cdot AB : 1 \cdot DC :: S : S', \quad \text{wherefore}$$

$$\begin{aligned} \frac{\sin(i-r)}{\sin(i+r)} &= \frac{\mu \cdot DC - AB}{\mu \cdot DC + AB} \cdot \frac{\mu}{\mu} \\ &= \frac{\mu^2 S' - S}{\mu^2 S' + S} \quad \dots \dots \dots (6) \end{aligned}$$

It may be of interest to first mention some minor consequences of these formulæ. At the incidence  $\tan^{-1} \mu$ ,  $S = S'$ , therefore (5) vanishes and (6) becomes  $(\mu^2 - 1)/(\mu^2 + 1)$ . When  $S = \mu S'$  (normal incidence) both (5) and (6) reduce to  $(\mu - 1)/(\mu + 1)$ . But, when  $\mu S = S'$ , (6) becomes  $(\mu^3 - 1)/(\mu^3 + 1)$  and (5) reduces to  $(1 - \mu)/(1 + \mu)$ . The latter is an interesting ratio of  $S$  to  $S'$ , for when the incident light is plane polarized perpendicular to the plane of incidence, we see that by simply reversing the normal incidence ratio of  $S$  to  $S'$  the reflected amplitude is equal but opposite in sign. The incidence where this occurs is found by writing  $\mu$  for  $\chi$  in (4), viz. :—

$$\sin i = \mu \sqrt{\frac{\mu^4 - 1}{\mu^6 - 1}} \quad \dots \dots \dots (7)$$

Another interesting ratio of  $S$  to  $S'$  occurs at  $i = 45^\circ$ , for when light incident at  $45^\circ$  is polarized  $\pm 45^\circ$  to the plane of incidence, then

$$\frac{\sin^2(i-r)}{\sin^2(i+r)} = \frac{\tan(i-r)}{\tan(i+r)} \quad \dots \dots \dots (8)$$

In the 8th edition of the *Ency. Britannica*, article "Optics," Sir David Brewster wrote: "It is a curious circumstance that . . . . in the action of all substances in turning round the planes of polarization, [by reflexion] at an incidence of  $45^\circ$ , the angle of rotation, when the plane of the polarized ray is  $\pm 45^\circ$ , is equal to the angle of refraction, while the new inclination [say  $\theta$ ] of the plane of polarization to the plane of reflection . . . . is equal to the deviation  $i - i'$ ." Of course, Brewster's proposition is easily deduced from (8) as the result of the particular angle of incidence. Now, when  $i = 45^\circ$ ,  $BA = AC = \mu$  (see fig. 1) and  $BD \cdot DC = (2\mu^2 - 1)^{\frac{1}{2}}$ , whence  $S : S' :: \mu^2 : (2\mu^2 - 1)^{\frac{1}{2}}$  and (5) and (6) become respectively

$$\frac{\mu^2 - (2\mu^2 - 1)^{\frac{1}{2}}}{\mu^2 + (2\mu^2 - 1)^{\frac{1}{2}}} \quad \text{and} \quad \frac{(2\mu^2 - 1)^{\frac{1}{2}} - 1}{(2\mu^2 - 1)^{\frac{1}{2}} + 1},$$

the former expression equalling the square of the latter.

Thus for all values of  $\mu$ , when the vibration of the light incident at  $45^\circ$  is symmetrically distributed as between being in and perpendicular to the plane of incidence, the reflected component in the plane of incidence is equal to the square of the reflected component perpendicular to that plane.

But the problem suggests itself, Is there not another angle of incidence, greater than  $\tan^{-1}\mu$ , where the same relation holds good? We know Fresnel's tangent formula is a diminishing ratio so far as the polarizing angle, and there had need be an incidence where (8) is the condition. But when  $i$  exceeds  $\tan^{-1}\mu$  the tangent ratio increases with  $i$  until at grazing incidence the tangent and sine ratios are equal. Therefore, in some part of the range of  $i$  beyond the polarizing angle we might reasonably look to find a recurrence of (8). Referring to fig. 1,  $AC : AB :: \mu : \mu/\tan i$ , whence

$$S : S' :: \mu^2/\tan i : \sqrt{(\mu^2 + \mu^2 \cot i - 1)}.$$

Substituting the latter ratio in (5) and (6) and equating these as in (8) we have

$$\left( \frac{(\mu^2 - \tan^2 i + \mu^2 \tan^2 i)^{\frac{1}{2}} - 1}{(\mu^2 - \tan^2 i + \mu^2 \tan^2 i)^{\frac{1}{2}} + 1} \right)^2 = \frac{\mu^2 - (\mu^2 - \tan^2 i + \mu^2 \tan^2 i)^{\frac{1}{2}}}{\mu^2 + (\mu^2 - \tan^2 i + \mu^2 \tan^2 i)^{\frac{1}{2}}},$$

whence  $\tan i = \pm 1$ . This result comes from what seems a perfectly general statement, yet it does not appear to give us any alternative to  $i=45^\circ$ , and one might be tempted to conclude that there was in fact no alternative. It was possible, however, that the statement could be made more general by raising it to a higher order, and so it proved, for on first squaring both members of the last equation and resolving for  $\tan i$  (the abridged operation involving a statement containing sixty-two terms) the result is  $\tan i = \pm 1$  or  $\pm [-\mu^2/(\mu^2 - 2)]^{\frac{1}{2}}$ . The latter pair of roots are what was sought. It will be seen at once that these new values of  $\tan i$  are real only when  $\mu < \sqrt{2}$ , thus we may conclude that there does not exist an alternative value of  $i$  for the condition (8) when  $\mu$  exceeds  $\sqrt{2}$ . Nevertheless, although we find an alternative angle of incidence for condition (8) when  $\mu < \sqrt{2}$ , yet we still have  $45^\circ$  as an adjunct, for when

$$\tan i = [-\mu^2/(\mu^2 - 2)]^{\frac{1}{2}}, \text{ then } \sin r = \pm \sqrt{\frac{1}{2}}, \text{ i. e., } r = 45^\circ.$$

The equation is

$$\tan^2 i = \frac{\sin^2 i}{1 - \sin^2 i} = \frac{\mu^2 \sin^2 r}{1 - \mu^2 \sin^2 r} = \frac{-\mu^2}{\mu^2 - 2},$$

whence  $\sin r = \pm \sqrt{\frac{1}{2}}$ .

No doubt, after knowing this, we can interpret the first result,  $\tan i = \pm 1$ , as meaning that condition (8) holds for  $\mu < 1$  as well as for  $\mu > 1$ , and thence deduce that it can only be true of  $\mu < 1$  when  $\mu > 1/\sqrt{2}$ , because, otherwise, there is total reflexion at  $i = 45^\circ$ , but this view was not at first apparent.

And  $\theta$  (see quotation from Brewster) equals  $i - r$  in this case also; for

$$\tan \theta = \frac{\tan(i - r)}{\tan(i + r)} \bigg/ \frac{\sin(i - r)}{\sin(i + r)},$$

and (8) being the condition

$$= \frac{\sin(i - r)}{\sin(i + r)} = \frac{\tan i - \tan r}{\tan i + \tan r},$$

but  $\tan r = 1$ ,  
therefore

$$\tan \theta = \frac{\tan i - 1}{\tan i + 1} = \tan(i - 45^\circ) = \tan(i - r).$$

The foregoing volume ratios lend themselves readily to the solution of the important problem of determining the angle of incidence required in order to reflect  $1/n$ th of the incident light both when one, and when two, surfaces of separation are involved. The formula to be deduced for the case when the incident light is unpolarized, or common, light, is of necessity complex, but we shall find some compensation for this in the interesting consequences of Fresnel's Theory not otherwise easily brought to light. We shall, first of all, dispose of the simpler cases where the incident light is polarized in, and perpendicular to, the plane of incidence, and of these, we may begin with Fresnel's tangent formula.

When  $1/n$ th the incident light is required to be reflected we have

$$\frac{1}{n} = \frac{\tan^2(i - r)}{\tan^2(i + r)} = \left( \frac{S - S'}{S + S'} \right)^2,$$

and writing  $S' = \chi S$ ,

$$\frac{1}{n} = \left( \frac{1 - \chi}{1 + \chi} \right)^2, \text{ whence } \chi = \frac{(\sqrt{n} \pm 1)^2}{n - 1} = \frac{\sqrt{n} + 1}{\sqrt{n} - 1} \text{ or } \frac{\sqrt{n} - 1}{\sqrt{n} + 1}.$$

We shall refer to the values of  $\chi$  as the  $+$  or  $-$   $\chi$  value according as the  $+$  or  $-$ , respectively, of the double sign is indicated.

Substituting these values of  $\chi$  in (3) and (4), we get

$$\tan i = \mu \sqrt{\frac{\left(\frac{(\sqrt{n+1})^2}{n-1}\right)^2 \mu^2 - 1}{\mu^2 - 1}}, \quad \sin i = \mu \sqrt{\frac{\left(\frac{(\sqrt{n+1})^2}{n-1}\right)^2 \mu^2 - 1}{\left(\frac{(\sqrt{n+1})^2}{n-1}\right)^2 \mu^4 - 1}}.$$

When  $n = \infty$  (as at the polarizing angle),  $\chi = 1$ , and  $\tan i = \mu$ , whichever of the pair of  $\chi$  values be employed.

Now, first consider  $\mu > 1$ . At normal incidence the ratio of light reflected is  $(\mu-1)^2/(\mu+1)^2$ ; therefore, make  $n = (\mu+1)^2/(\mu-1)^2$ , then, the  $+\chi$  value  $= \mu$ , and the  $-\chi$  value  $= \mu^{-1}$ . Substituting these  $\chi$  values in the expression for  $\sin i$  we get respectively

$$\sin i = \mu \sqrt{\frac{\mu^4 - 1}{\mu^6 - 1}} \text{ and } 0.$$

The latter sine value indicates normal incidence, and the former is identical with (7), which was shown to be the sine value of  $i$  when the ratio of reflected light is again equal to that reflected at normal incidence. But both  $\chi$  values were found to be applicable at the incidence  $\tan^{-1} \mu$ ; therefore, we should write the  $-\chi$  value in (3) or (4) for the range of  $i$  from normal incidence to  $\tan^{-1} \mu$ , and the  $+\chi$  value for the range from the latter angle to that whose sine is expressed by (7).

The  $+\chi$  value has also to be adopted for the remaining range of  $i$  to  $90^\circ$ , a range where the value of  $n$  must lie between  $(\mu+1)^2/(\mu-1)^2$  and 1. If  $n$  lie within these limits, the adoption of the  $-\chi$  value leads to an imaginary expression for  $\tan i$ , and to impossible values of  $\sin i$ . The unreality of  $\tan i$  under these conditions may be shown as follows:—Let  $n = (\mu+1-h)^2/(\mu-1+h)^2$  where  $h$  may have any value between 0 and 1, thus covering the case of any value of  $n$  between  $(\mu+1)^2/(\mu-1)^2$  and 1. Substituting  $(\mu+1-h)/(\mu-1+h)$  for  $\sqrt{n}$  in the  $-\chi$  value, we find

$$\chi = (1-h)/\mu$$

and

$$\tan i = \mu \sqrt{\frac{h(h-2)}{\mu^2 - 1}}.$$

The numerator,  $h(h-2)$ , is negative for any value of  $h < 2$ , and  $\mu^2 - 1$  is positive when  $\mu > 1$ , wherefore the expression is imaginary. In similar manner it can be shown that the

$+\chi$  value furnishes real values of  $\tan i$  in the range of  $i$  under consideration.

In the case of  $\mu < 1$  the conditions for employing the  $+$  or  $-\chi$  value are reversed. In showing this, it has first to be noted that  $1/n$  can only have a meaning when it is taken as positive, and that  $\mu$  being  $< 1$ ,  $(\mu + 1)/(\mu - 1)$  is negative. Therefore, let  $\sqrt{n} = (1 + \mu)/(1 - \mu)$ , and we find the  $+\chi$  value  $= \mu^{-1}$  and the  $-\chi$  value  $= \mu$ . Substituting these values of  $\chi$  as before,  $\sin i =$  respectively 0 and  $\mu(\mu^4 - 1)^{\frac{1}{2}}/(\mu^6 - 1)^{\frac{1}{2}}$ , the two values of  $\chi$  thus occurring in an order opposite to that which held in the case of  $\mu > 1$ . Also, in the remaining range of  $i$ , from where  $S' = \mu S$  to total reflexion, it is easily shown that the  $-\chi$  value has to be adopted. Similarly, it can be shown that the adoption of the  $-\chi$  value furnishes real tangent values for this range of  $i$  when  $\mu < 1$ .

Therefore, when the light vibrates in the plane of incidence, in order to reflect  $1/n$ th at a plane interface, the angle of incidence is determined by (3) or (4) where  $\chi = (\sqrt{n} \pm 1)^2/(n - 1)$ . When  $\mu > 1$ , the minus sign applies to the range of  $i$  from normal incidence to  $\tan^{-1}\mu$  and the plus sign to the range of  $i$  from the latter angle to grazing incidence. This may be referred to the value of  $n$  by stating that when  $n < (\mu + 1)^2/(\mu - 1)^2$  the  $+\chi$  value should be adopted, and when

$$n = \text{or} > (\mu + 1)^2/(\mu - 1)^2,$$

then both  $\chi$  values may be employed, thus determining two incidences where the reflected light is equal. When  $\mu < 1$ , the order of adoption of these signs has to be exactly reversed.

The reflexion at one interface only has, so far, been dealt with, but towards the end of the paper it will be shown how to determine  $i$  in order to reflect or transmit a given ratio of the incident light when both surfaces of a plate are involved. To provide a reference for that case, it is here necessary to show that when  $1/n$ th the incident light is reflected at the first surface of a homogeneous isotropic refracting medium bounded by parallel planes, then  $1/n$ th of the refracted light is reflected at the second surface.

If  $\mu$  be the refractive index of the second medium with respect to the first,  $\mu^{-1}$  is the index of the first with respect to the second. For convenience, let a single value of  $\chi$  in terms of  $n$  be employed for the incident ray, but we must remember the alternative  $\chi$  value must then be adopted for the refracted ray. We have, then,  $1/n$ th light incident on



first surface reflected at an incidence of

$$\sin^{-1} \mu \left[ \left( \frac{\sqrt{n+1}}{\sqrt{n-1}} \right)^2 \mu^2 - 1 \right]^{\frac{1}{2}} / \left[ \left( \frac{\sqrt{n+1}}{\sqrt{n-1}} \right)^2 \mu^4 - 1 \right]^{\frac{1}{2}}$$

and  $1/n$ th of the refracted ray incident on second surface at an incidence

$$\sin^{-1} \frac{1}{\mu} \left[ \left( \frac{\sqrt{n-1}}{\sqrt{n+1}} \right)^2 \frac{1}{\mu^2} - 1 \right]^{\frac{1}{2}} / \left[ \left( \frac{\sqrt{n-1}}{\sqrt{n+1}} \right)^2 \frac{1}{\mu^4} - 1 \right]^{\frac{1}{2}}.$$

We shall see that the latter expression is simply the former transferred from the incident to the refracted ray. Multiplying the numerator and denominator of the former expression in the surd by  $-(\sqrt{n-1})^2/\mu^4(\sqrt{n+1})^2$ , we get

$$\sin i = \left[ \left( \frac{\sqrt{n-1}}{\sqrt{n+1}} \right)^2 \frac{1}{\mu^2} - 1 \right]^{\frac{1}{2}} / \left[ \left( \frac{\sqrt{n-1}}{\sqrt{n+1}} \right)^2 \frac{1}{\mu^4} - 1 \right]^{\frac{1}{2}}.$$

But  $\mu^{-1} \sin i = \sin r$ , therefore

$$\sin r = \frac{1}{\mu} \left[ \left( \frac{\sqrt{n-1}}{\sqrt{n+1}} \right)^2 \frac{1}{\mu^2} - 1 \right]^{\frac{1}{2}} / \left[ \left( \frac{\sqrt{n-1}}{\sqrt{n+1}} \right)^2 \frac{1}{\mu^4} - 1 \right]^{\frac{1}{2}},$$

thus proving the proposition.

When the incident light is polarized in the plane of incidence—the undulations being perpendicular to that plane—the equation is

$$1/n = \sin^2(i-r) / \sin^2(i+r) = (\mu^2 S' - S)^2 / (\mu^2 S' + S)^2.$$

Let  $S' = \chi S$ , then  $1/n = (\mu^2 \chi - 1)^2 / (\mu^2 \chi + 1)^2$ , whence

$$\chi = \frac{(\sqrt{n+1})^2}{\mu^2(n-1)} = \frac{\sqrt{n+1}}{\mu^2(\sqrt{n-1})} \quad \text{or} \quad \frac{\sqrt{n-1}}{\mu^2(\sqrt{n+1})}.$$

The application of the proper value of  $\chi$  in this case is not so complex. The  $+\chi$  value has to be employed when  $\mu > 1$ , and the  $-\chi$  value when  $\mu < 1$ .

Also, when  $1/n$ th the incident light is reflected at the first surface of a refracting plate, then  $1/n$ th of the refracted ray is reflected at the posterior surface. This can be shown in the same manner as for light vibrating in the plane of incidence.

The reflexion of common light is usually treated as if the light were composed of two equal rays polarized in and perpendicular to the plane of incidence; hence,

$$\frac{1}{n} = \frac{1}{2} \left( \frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)} \right).$$

314 Mr. R. B. Sangster on some Consequences of  
Substituting the volume formulæ and writing  $\chi S$  for  $S'$ ,

$$\frac{1}{n} = \frac{1}{2} \left[ \left( \frac{\mu^2 \chi - 1}{\mu^2 \chi + 1} \right)^2 + \left( \frac{1 - \chi}{1 + \chi} \right)^2 \right].$$

In expressing the values of  $\chi$  in this equation some abbreviation will be an advantage.

Let  $2n(\mu^2 - 1)^2 - n^2(\mu^4 - 6\mu^2 + 1) = p$ , then

$$\chi^2 - \frac{\mu^2 + 1 \pm \sqrt{p}}{\mu^2(n-1)} \chi = -\frac{1}{\mu^2}.$$

The next step is to add the square of half the coefficient of  $\chi$  to both sides of the equation, and, for future reference, it has to be noted that in making this addition,  $\sqrt{p}$  in the coefficient of  $\chi$  must have the same sign simultaneously attributed to it in both sides. Again abbreviating, let

$$(\mu^2 + 1 \pm \sqrt{p})^2 - 4\mu^2(n-1)^2 = q,$$

then

$$\chi = \frac{\mu^2 + 1 \pm \sqrt{p} \pm \sqrt{q}}{2\mu^2(n-1)}.$$

In dealing with this formula numerically it is generally more convenient to write the equivalent of  $p$  and  $q$  as

$$p = (2n - n^2)(\mu^4 + 1) - 2\mu^2(2n - 3n^2),$$

$$q = (2n - n^2 + 1)(\mu^4 + 1) + 2\mu^2(2n + n^2 - 1) \pm 2(\mu^2 + 1)\sqrt{p}.$$

It will be noticed that  $\sqrt{p}$  occurs twice in the values of  $\chi$ , but the origin of the double occurrence in the process of extracting the roots, demands that a similar sign, either + or -, shall be attached to the two occurrences. There are, therefore, four roots to the equation.

We have one pair of values of  $\chi$  in which  $\sqrt{q}$  is positive; these are applicable to the case of  $\mu > 1$ . The pair in which  $\sqrt{q}$  is negative are for use when  $\mu$  is  $< 1$ . In order to show this, write  $\mu = 1$  in the values of  $\chi$  and in the sine formula (4). When  $-\sqrt{p}$  is adopted, the result is  $\chi = -1$ , which is an impossible value of  $\chi$ , since  $\chi$  must always be positive, and the reason for this result will be seen presently. When, however, we adopt  $+\sqrt{p}$ , then  $+\sqrt{q}$  makes

$$\chi = (\sqrt{n+1})/(\sqrt{n-1}),$$

and  $-\sqrt{q}$  gives  $\chi = (\sqrt{n-1})/(\sqrt{n+1})$ , and in both cases the resulting angle is  $90^\circ$ . Now it is obvious that as  $i$  approaches indefinitely near to  $90^\circ$ ,  $S'/S \equiv \chi$  is  $>$  or  $<$  unity according as  $\mu$  is  $>$  or  $<$  unity. But  $+\sqrt{q}$  gives

us  $\chi = (\sqrt{n+1})/(\sqrt{n-1})$ , which is  $<1$  whatever positive integral value  $n$  may have, hence  $+\sqrt{q}$  applies to the case of  $\mu > 1$ . Similarly,  $-\sqrt{q}$  applies to  $\mu < 1$ .

It has now to be shown that the negative sign of  $\sqrt{p}$  is applicable only when the value of  $\mu$  lies beyond the limits  $2 \pm \sqrt{3}$ , and some statement of the reason for this will enable the argument to be more easily followed.

Fresnel's tangent formula shows that the reflexion of light vibrating in the plane of incidence diminishes from normal incidence to the incidence  $\tan^{-1}\mu$ , but his sine formula, for the vibration perpendicular to that plane, gives a continual increase of the light reflected as  $i$  increases. The combined formula for common light gives ratios of reflected light which generally increase with  $i$  throughout the whole range of  $i$  in which the reflected light can vary. This statement regarding common light, however, requires to be qualified to the extent that it only holds good while  $\mu$  lies within the limits  $2 \pm \sqrt{3}$ . When  $\mu$  lies beyond these limits, the quantity of reflected common light diminishes at first as  $i$  increases from  $0^\circ$ . We have seen that the ratio of reflected common light, in terms of  $\chi$  and  $\mu$ , is

$$f(\chi) = \frac{1}{2} \left[ \left( \frac{\mu^2\chi - 1}{\mu^2\chi + 1} \right)^2 + \left( \frac{1 - \chi}{1 + \chi} \right)^2 \right];$$

and differentiating this expression we get

$$f'(\chi) = \frac{2\chi(1 - \mu^2\chi^2)(\mu^4 - 6\mu^2 + 1) + 2(\mu^2 + 1)(\mu^4\chi^4 - 1)}{(\mu^2\chi^2 + \mu^2\chi + \chi + 1)^3}.$$

At normal incidence  $\chi = \mu^{-1}$ , and we find  $f'(\mu^{-1}) = 0$ , showing that the gradient of  $f(\chi)$  at normal incidence  $= 0$ .

But,

$$f'(\chi) = 4[4\mu^6\chi^4 + 2\mu^2\chi^2(\mu^2\chi^2 - 2)(\mu^4 - 6\mu^2 + 1) + \mu^2\chi(\mu^2 + 1)(2\mu^2\chi^2 - \mu^4\chi^4 + 8) - \chi(\mu^6 + 1) + 2(\mu^4 + 1)] \div (\mu^2\chi^2 + \mu^2\chi + \chi + 1)^4$$

$$\text{and} \quad f''(\mu^{-1}) = \frac{-4\mu^3(\mu^2 - 4\mu + 1)}{(\mu + 1)^4};$$

if  $f''(\mu^{-1}) = 0$ , then  $\mu = 2 \pm \sqrt{3}$ .

Therefore,  $f''(\mu^{-1})$  changes from positive to negative as  $\mu$  passes out through the limits  $2 \pm \sqrt{3}$ ; wherefore, when  $\mu$  lies beyond these limits,  $f(\chi)$  diminishes at first as  $\chi$  increases from  $\mu^{-1}$ , or, as  $i$  departs from the normal.

This decrease in  $f(\chi)$  with increase of  $\chi$  can only be expected to continue through a limited range and the following

zero values of  $f'(\chi)$  will tell us where the turning values of  $f(\chi)$  (obviously minima) occur:—

$$f' \left( \frac{\mu^4 - 6\mu^2 + 1 \pm \sqrt{(\mu^4 - 8\mu^2 + 1)^2 - 36\mu^4}}{2\mu^2(\mu^2 + 1)} \right) = 0.$$

These are complex values of  $\chi$ , and it will presently be seen how they are obtained; meantime, it may be pointed out that they are real values only when the quantity  $(\mu^4 - 8\mu^2 + 1)^2 - 36\mu^4$  is positive, which requires  $\mu$  to lie outside the limits  $2 \pm \sqrt{3}$ . It should also be noted that they are values of  $\chi$  which have to be written in the sine formula (4) in order to determine the critical angle of incidence where minimum reflexion occurs, and it has been found, on numerical trial, that the + sign of the pair of signs has to be adopted for  $\mu > 1$ , otherwise we are confronted with an unreal sine value.

We can now determine the proper application of the signs of  $\sqrt{p}$ . It was shown that the two occurrences of  $\sqrt{p}$  in the value of  $\chi$  must have a similar sign attached for any legitimate value of  $\chi$ , so we need only consider the sign of  $\sqrt{p}$  as it occurs in  $q$ .

Let  $q$  be equated to zero, then,  $n = 1$  or  $(\mu + 1)^2/(\mu - 1)^2$ , according as + or  $-\sqrt{p}$  be adopted. If  $p$  be equated to zero,  $n = 0$  or  $2(\mu^2 - 1)^2/(\mu^4 - 6\mu^2 + 1)$ . (Incidentally, this limit to the value of  $n$ , as it occurs in  $p$ , holds good only while  $n$  is positive; whence  $\mu^4 - 6\mu^2 + 1 = 0$ , or  $\mu = 1 \pm \sqrt{2}$ , determines the convergency limits of its application. If  $\mu$  lie within the limits  $1 \pm \sqrt{2}$ ,  $\sqrt{p}$  is real however great we suppose  $n$  to be.) Therefore, in order that  $p$  and  $q$  may vanish simultaneously,  $n$  must equal both

$$(\mu + 1)^2/(\mu - 1)^2 \text{ and } 2(\mu^2 - 1)^2/(\mu^4 - 6\mu^2 + 1),$$

which can be true only when  $\mu = 2 \pm \sqrt{3}$ , thus making  $n = (\mu + 1)^2/(\mu - 1)^2 = 3$ . These are the values of  $\mu$  that reflect one-third the incident light at normal incidence, and we have seen that they are turning values in  $f''(\mu^{-1})$ .

Therefore, when  $\mu$  lies outside the limits  $2 \pm \sqrt{3}$  we need two values of  $\chi$  for values of  $n$  greater than  $(\mu + 1)^2/(\mu - 1)^2$ , similarly to what was required in the reflexion of light vibrating in the p' plane of incidence, and it is in that case that both signs of  $\sqrt{p}$  have to be employed.

When  $n = 2(\mu^2 - 1)^2/(\mu^4 - 6\mu^2 + 1)$ ,  $p$  vanishes,

$$\sqrt{q} = \frac{(\mu^2 + 1) \sqrt{(\mu^4 - 8\mu^2 + 1)^2 - 36\mu^4}}{\mu^4 - 6\mu^2 + 1}$$

and

$$\chi = \frac{\mu^4 - 6\mu^2 + 1 \pm \sqrt{(\mu^4 - 8\mu^2 + 1)^2 - 36\mu^4}}{2\mu^2(\mu^2 + 1)}. \quad (9)$$

These are values of  $\chi$  that were shown to make  $f(\chi)$  a minimum, and they are arrived at by ascribing to  $n$  a value such that  $p$  shall vanish, thus furnishing one limit for the use of  $-\sqrt{p}$  and  $+\sqrt{p}$ .

Again, the ratio of light reflected at normal incidence is  $(\mu - 1)^2/(\mu + 1)^2$ , and if we write  $(\mu + 1)^2/(\mu - 1)^2$  for  $n$ , as  $n$  occurs in  $p$  and  $q$ , then

$$\sqrt{p} = \mu^2 + 1 - 8\mu^2/(\mu - 1)^2;$$

and if  $-\sqrt{p}$  be adopted, then

$$q = 0, \quad \chi = \mu^{-1}, \quad \sin i = 0.$$

This value,  $(\mu + 1)^2/(\mu - 1)^2$ , of  $n$  determines the other limit of  $n$  for which  $-\sqrt{p}$  can be employed; therefore, these limits show that the negative sign of  $\sqrt{p}$  is applicable to the range of  $i$  from normal incidence to the incidence where minimum reflexion occurs.

But, if we make the latter substitution for  $n$  in  $p$  and  $q$  and adopt  $+\sqrt{p}$ , then,

$$\sqrt{q} = 2[(\mu^2 - 1)^2 - 4\mu^2(\mu + 1)^2/(\mu - 1)^2]^{\frac{1}{2}},$$

an expression, however, which is real only when  $\mu$  lies outside the limits  $2 \pm \sqrt{3}$ . This is the value of  $\sqrt{q}$  (in conjunction with  $n = (\mu + 1)^2/(\mu - 1)^2$  throughout the  $\chi$  value) that is required in order to determine the other angle of incidence where the light reflected is equal to that reflected at normal incidence; and in (9) we found a limit to the use of the positive sign of  $\sqrt{p}$  at the incidence where minimum reflexion occurs, hence the  $+$  sign of  $\sqrt{p}$  is applicable to the range of  $i$  from where minimum reflexion occurs to grazing incidence.

The graphs in figs. 2 and 3 will usefully illustrate these varying relations of  $\sqrt{p}$  to  $q$  when  $\mu >$  and  $< 2 + \sqrt{3}$ . Writing

$$q = \frac{(2n - n^2 + 1)(\mu^4 + 1) + 2\mu^2(2n + n^2 - 1)}{2(\mu^2 + 1)} \pm \sqrt{p},$$

in fig. 2 the graphs,  $F(n)=q-\sqrt{p}$ , and  $F(n)=\sqrt{p}$  are shown for  $\mu=2$ ; and in fig. 3, the same graphs when  $\mu=4$ .

Fig. 2.

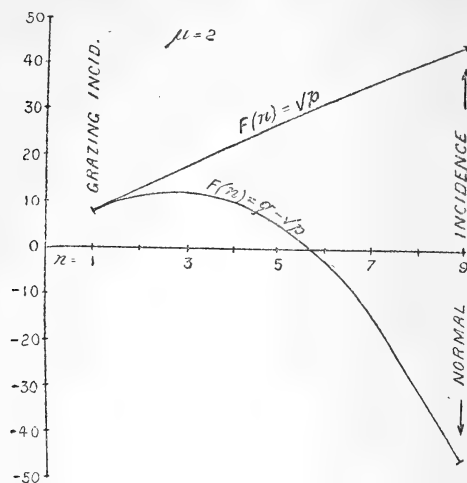
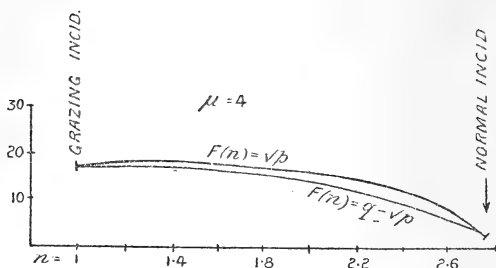


Fig. 3.



A numerical example of these formulæ may also be of interest. When  $\mu=2+\sqrt{3}$  (approximately,  $3.732$ ), the normal is the incidence of minimum reflexion. When  $\mu=4$ , minimum reflexion occurs at  $i=57^{\circ}28'$ , showing how quickly the minimum moves away from the normal with increase of  $\mu$ ; but when  $i=65^{\circ}36'$ , the light reflected is again equal to that reflected at normal incidence.

Doubtless, these high values of  $\mu$  are found only in the region of metallic reflexion where metallic absorption has to be taken into account and where Fresnel's formula has to be dealt with in a modified form, and it is only in order to discuss the significance of  $\pm\sqrt{p}$  that we are compelled for the time to treat these high values of  $\mu$  as if they applied to

ordinary transparent media. In this connexion, it is of interest to find that so long ago as 1830 Mr. Potter discovered that the light reflected by steel diminishes with increase of  $i$  for a considerable range from normal incidence.

The transference of the formula from the incident ray to the ray refracted into a plane-parallel plate is necessarily somewhat tedious in the case of common light. When  $\mu$  is the index of the second medium with respect to the first,  $\mu^{-1}$  is the index of the first with respect to the second. Assuming  $\mu > 1$ , the + sign of  $\sqrt{q}$  has to be adopted in the  $\chi$  value and we have  $1/\mu$ th the incident ray reflected when

$$\sin i = \sqrt{\frac{(\mu^2 + 1 \pm \sqrt{p + \sqrt{q}})^2 - 4\mu^2(n-1)^2}{(\mu^2 + 1 \pm \sqrt{p + \sqrt{q}})^2 - 4(n-1)^2}}.$$

Multiplying the numerator and denominator in the surd by  $(\mu^2 + 1 \pm \sqrt{p - \sqrt{q}})^2$ , we obtain

$$\sin i = \sqrt{\frac{[(\mu^2 + 1 \pm \sqrt{p})^2 - q]^2 - 4\mu^2(n-1)^2(\mu^2 + 1 \pm \sqrt{p - \sqrt{q}})^2}{[(\mu^2 + 1 \pm \sqrt{p})^2 - q]^2 - 4(n-1)^2(\mu^2 + 1 \pm \sqrt{p - \sqrt{q}})^2}}.$$

But,  $q = (\mu^2 + 1 \pm \sqrt{p})^2 - 4\mu^2(n-1)^2$ ,

therefore the term

$$[(\mu^2 + 1 \pm \sqrt{p})^2 - q]^2 = 16\mu^4(n-1)^4$$

and

$$\sin i = \sqrt{\frac{4\mu^4(n-1)^2 - \mu^2(\mu^2 + 1 \pm \sqrt{p - \sqrt{q}})^2}{4\mu^4(n-1)^2 - (\mu^2 + 1 \pm \sqrt{p - \sqrt{q}})^2}}.$$

Multiplying the numerator and denominator in the surd by  $-\mu^{-4}$ , taking care to include  $\sqrt{p}$  and  $\sqrt{q}$  in the operation, we get

$$\begin{aligned} \sin i &= \sqrt{\frac{(\mu^{-2} + 1 \pm \sqrt{p - \sqrt{q}})^2 \mu^2 - 4(n-1)^2}{(\mu^{-2} + 1 \pm \sqrt{p - \sqrt{q}})^2 - 4(n-1)^2}} \\ &= \sqrt{\frac{\left(\frac{\mu^{-2} + 1 \pm \sqrt{p - \sqrt{q}}}{2\mu^{-2}(n-1)}\right)^2 \frac{1}{\mu^2} - 1}{\left(\frac{\mu^{-2} + 1 \pm \sqrt{p - \sqrt{q}}}{2\mu^{-2}(n-1)}\right)^2 \frac{1}{\mu^4} - 1}}. \end{aligned}$$

and  $\mu^{-1} \sin i = \sin r$ , therefore

$$\sin r = \frac{1}{\mu} \sqrt{\frac{\left(\frac{\mu^{-2} + 1 \pm \sqrt{p - \sqrt{q}}}{2\mu^{-2}(n-1)}\right)^2 \frac{1}{\mu^2} - 1}{\left(\frac{\mu^{-2} + 1 \pm \sqrt{p - \sqrt{q}}}{2\mu^{-2}(n-1)}\right)^2 \frac{1}{\mu^4} - 1}}.$$

This value of  $\sin r$  is what we should have had for  $\sin i$ , if, in the first instance, we had written  $\mu^{-1}$  for  $\mu$ , and  $-\sqrt{q}$  instead of  $+\sqrt{q}$  as is required for  $\mu < 1$ , and we see it is the sine angle of the refracted ray. Therefore, in the case of common light also, when  $1/n$ th the light incident on a plane-parallel plate is reflected at the first surface,  $1/n$ th the refracted ray is reflected at the second surface.

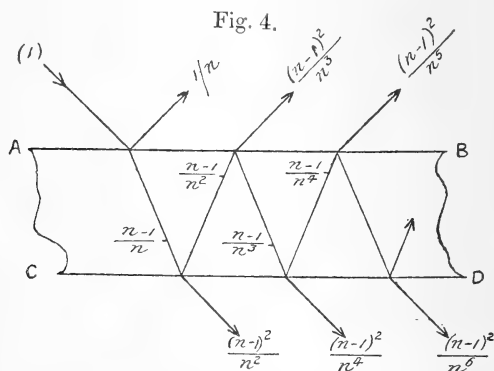
It will be observed that this is equivalent to saying that

$$\frac{\sin^2(i-r)}{\sin^2(i+r)} + \frac{\tan^2(i-r)}{\tan^2(i+r)} = \frac{\sin^2(r-i)}{\sin^2(r+i)} + \frac{\tan^2(r-i)}{\tan^2(r+i)},$$

an obvious enough equation; but the individual demonstrations by means of the  $1/n$ th formulæ are also necessary in view of the varying alterations of sign required in these when  $\mu$  is  $>$  or  $< 1$ .

The refracted ray is reflected many times to and fro in the interior of the refracting medium from surface to surface, but if the reflecting surfaces are plane-parallel, the angle of incidence is the same at each reflexion, and if  $1/n$ th is reflected at the first interior reflexion,  $1/n$ th will be reflected at each successive contact with a surface. In consequence, there is a simple way of determining the angle of incidence in order to reflect or transmit a definite proportion of the incident light when the two surfaces of a plate are involved.

Suppose it is required to reflect  $1/m$ th the light incident on a transparent, homogeneous, isotropic refracting medium, bounded by parallel planes, where the repeated reflexions and transmissions at both surfaces have to be taken into account. When, under these conditions,  $1/m$ th the incident ray is reflected back into the first medium, let  $1/n$  be the ratio reflected at the first incidence on the first surface of separation; what we need is the relation of  $m$  to  $n$ .



Referring to fig. 4, where AB and CD are the surfaces of the refracting medium, (1) is the incident ray. At the first



incidence  $1/n$ th is reflected and  $1-1/n$  enters the second medium;  $1/n$ th of the latter, or,  $(n-1)/n^2$  of (1), is then reflected at the second surface to again fall on the interior of the first surface, where  $1/n$ th of  $(n-1)/n^2$  is reflected and  $(n-1)/n^2 - (n-1)/n^3$  is transmitted to augment the  $1/n$ th reflected at first incidence. The interior reflected ray returns repeatedly to the first surface where the quantity transmitted back diminishes  $n^2$  times each time in succession. The result is that

$$\frac{1}{m} = \frac{1}{n} + \frac{(n-1)^2}{n^3} + \frac{(n-1)^2}{n^5} + \dots + \frac{(n-1)^2}{n^t},$$

where  $t$  is the total number of reflexions to be taken into account. The sum of the series is  $(2n^t - n + 1)/n^t(n+1)$ , and if  $t$  is large it will not be an easy problem to determine  $n$  in terms of  $m$ . But, if  $t$  is large, it is better to write  $t = \infty$ , when the sum becomes  $2/(n+1)$ , whence  $n = 2m - 1$ . This can be done without appreciable error when the incidence is not too oblique, because all the terms to infinity after that involving  $t$  only sum-up to

$$\frac{2}{n+1} - \frac{2n^t - n + 1}{n^t(n+1)} = \frac{(n-1)^2}{n^t(n^2-1)},$$

a sum which is less than the last single term required when  $n^2 > 2$ .

Therefore, when  $1/m$ th the incident light is required to be reflected from a refracting plate, the corresponding ratio required to be reflected at first incidence is  $1/(2m-1)$ , and substituting the value of the denominator of this expression for  $n$  in the appropriate value of  $\chi$ , we can determine the necessary angle of incidence.

At normal incidence, the ratio of reflected light at first incidence is  $1/n = (\mu-1)^2/(\mu+1)^2$ , but if we add the effect of the innumerable to-and-fro reflexions in the interior of a plate, the total quantity reflected back into the first medium is  $1/m = (\mu-1)^2/(\mu^2+1)$ . At normal incidence, for  $\mu = 1.5$ ,  $1/n = 1/25$ , while  $1/m = 1/13$ . When

$$\tan i = \mu, \quad 1/m = (\mu^2-1)^2/(\mu^4+1).$$

The incidence necessary in order to transmit a given ratio through the plate can be found in a similar manner. Referring to fig. 4, we get the series

$$\frac{1}{m'} = \frac{(n-1)^2}{n^2} + \frac{(n-1)^2}{n^4} + \frac{(n-1)^2}{n^6} + \dots + \frac{(n-1)^2}{n^t},$$

where  $1/m'$  is the ratio of transmitted to incident light and  $t$

the total number of reflexions taken into account. Summing this series, we get  $1/m' = 1 - (2n^t + n - 1)/n^t(n + 1)$ , or, if  $t$  is assumed  $= \infty$ ,  $1/m' = (n - 1)/(n + 1)$ ; whence

$$n = (m' + 1)/(m' - 1).$$

It will be observed it is only on the assumption of there being an infinity of interior reflexions that we get  $1/m' = 1 - 1/m$ .

In concluding this paper I venture the tentative suggestion that the  $\mu$  values  $1 \pm \sqrt{2}$  found in this investigation mark a transition stage in Fresnel's Reflexion formula. The hypothesis would be that when  $\mu$  lies outside these limits, some modification of the general formula has to be introduced such as is found to be well enough marked in the case of metallic reflexion.

XXXII. *On Polarization of Undiffracted Long-waved Heat Rays by Wire Gratings.* By H. DU BOIS and H. RUBENS\*.

NOTATION.

$a, a'$ , constant of grating.	$Q$ , central transmissibility.
$b, b'$ , slit-widths.	$Q_s$ , transmissibility ( $\perp$ polar. rays).
$d$ , diameter of wire.	$Q_p$ , transmissibility ( $\parallel$ polar. rays).
$\beta$ , angle of inclination.	$Q_m$ , mean transmissibility.
$\sqrt{\phantom{x}}$ , polarization azimuth.	$R_s$ , reflecting power ( $\perp$ polar. rays).
$n^2$ , transmissibility ratio.	$R_p$ , reflecting power ( $\parallel$ polar. rays).

I. INTRODUCTION.

§ 1. **T**WENTY years ago† one of us investigated, among others, three silver wire gratings ( $45\mu < d < 180\mu$ ) corresponding to the interval

$$20 < b'/\lambda < 100,$$

which produced in the visible region a partial polarization of the undiffracted central image at right angles to the wires. The apparent slit-width  $b'$  may be decreased and the polarization increased by inclining the grating up to  $50^\circ$ ; the effect proved to be nearly independent of the thickness of the wire; further, it increased from the violet to the red up to about 13 per cent. No appreciable differences of phase were evident. Unindented rulings ( $> 1\mu$ ) made on films of deposited platinum also polarize perpendicularly, but much less and with smaller dispersion. In addition, the reflected

\* Communicated by the Authors.

† H. du Bois, *Verh. d. Phys. Ges. Berlin*, x. p. 71 (1891); *Wied. Ann.* xlv. p. 548 (1892), xlviii. p. 546 (1893).

light from such metallic layers is also polarized at right angles. On the other hand, the ordinary diamond-ruled glass gratings polarize, in the Hertzian sense, up to 6 per cent.; they are, of course, not so well defined as the regular wire gratings. The latter also produce ellipticity.

In continuing this work Dr. Franz Braun\* investigated platinum, copper, iron, and gold wire gratings immersed in air, carbon bisulphide, methyl alcohol, and benzene. The ratio of transmissibility  $n^2 = Q_s/Q_p$  diminished with decreasing wave-length, no matter whether as a consequence of change of colour or of the refractive index of the surrounding medium. Increase of temperature up to  $250^\circ$  had no perceptible influence. The sense of the polarization was always the same also when, for example, the gold wires were brought as near to one another as possible; on the other hand, no effects of any sort were observed with quartz threads.

Similar experiments were carried out by Prof. Ambrohn† with gratings made of sewing-needles, prepared in the same way as by v. Mohl and Hofmeister. He repeated Fizeau's experiment with rulings less than  $0.1\ \mu$  in width on a very thin silver film; he found, among other results, that many of these rulings readily  $\parallel$  polarize red and yellow light, while, on the other hand, blue or violet light is transmitted  $\perp$  polarized.

§ 2. In 1893 we investigated, in the infra-red, eight gratings of platinum, copper, iron, gold, and silver wire, the apparent slit-widths  $b'$  of which varied between 10 and  $60\ \mu$ ; since wave-lengths from  $0.8$  to  $5\ \mu$  were used, this investigation thus extended over the region

$$2 < b'/\lambda < 75,$$

while in Hertz's analogous investigation  $b'/\lambda$  was only  $0.05$ .

The ratio of transmissibility  $n^2 = Q_s/Q_p$  could, in pursuance of the optical measurements, be determined as a function of the wave-length. In the case of each of the five metals it very soon reached a maximum in the infra-red ( $n^2 > 1$ , up to nearly  $1.5$ ) with wave-lengths  $0.8$ – $1.3\ \mu$ : an inversion ( $n^2 = 1$ ) occurred later of such a kind that from that point onwards the polarization of longer waves followed according to the Hertzian sense ( $n^2 < 1$ ).

For each metal the ratio of the characteristic wave-lengths corresponding to the above-mentioned maximum and inversion points was about  $1 : 2.35$ , and appeared independent of the

\* Franz Braun, Inaug.-Diss., Berlin 1896.

† H. du Bois and H. Rubens, Wied. Ann. xlix. p. 593 (1893), further on referred to as *l. c.*

thickness of the wire and apparent slit-width;  $n^2$  seemed to depend only on the latter, at least within the region investigated. This simple course was in accordance with expectations, for in the infra-red, apart from the more favourable ratio  $b'/\lambda$ , the molecular periods of the metals play only a small part, while in the visible part of the spectrum they completely dominate their behaviour.

After some experiments on partial polarization by means of ruled gratings had been described in the first publication on Reststrahlen\*, we applied a platinum-wire grating to the Reststrahlen of fluorite and rocksalt†. These were polarized by reflexion from glass and quartz plates at the polarizing angle. It was found also in the long-wave region that a decrease in the ratio of transmissibility took place with increasing wave-length, thus showing a closer approach to complete Hertzian polarization.

§ 3. Sir J. J. Thomson‡ has calculated the polarization through a grating the interspaces of which are small in comparison with the wave-length, as well as the scattering of light by a metallic or dielectric cylinder.

Lord Rayleigh§ has solved the mathematical problem of the transmission of wave disturbances through openings in plane thin infinite conducting sheets. He found that a narrow slit—of width infinitely small in proportion to the wave-length—parallel to the electric vibration transmits a very much smaller quantity than the amount reflected by a conductor which fits exactly in the same slit. He also investigated the influence of ellipsoidal and elliptical cylindrical obstacles of dimensions again infinitely small in comparison with the wave-length,—a problem, the solution of which we had already pointed out as desirable (*l. c.* § 33).

With regard to such calculations Prof. Lamb|| investigated the reflexion and transmission of electric waves through metallic gratings, again under the assumption that the distance of the strips from one another was small in comparison with the wave-length; otherwise no special conditions were postulated.

\* H. Rubens and E. F. Nichols, *Wied. Ann.* lx. p. 418 (1897).

† H. du Bois and H. Rubens, *Verh. d. Deutsch. Phys. Ges.* vi. p. 77 (1904); in the table on p. 81 the value of  $Q_p$  for  $25.5\mu$  should be 0.365 not 0.265, due to a printers' error).

‡ J. J. Thomson, *Rec. Res. in Electr. & Magn.* §§ 359–368, p. 425 *seq.* Oxford, 1893. The corresponding calculations for conducting and dielectric spheres, of late investigated by various authors, are only indirectly connected with the grating effect.

§ Lord Rayleigh, *Phil. Mag.* [5] xliii. p. 259, xliv. p. 28 (1897).

|| H. Lamb, *Proc. Math. Soc. London*, xxix. p. 523 (1893); *Beiblätter*, xxiii. p. 277 (1899).

On continuing the Fizeau-Ambrohn investigation Prof. Ferd. Braun\* produced a partial Hertzian polarization of light by means of certain structural appliances which were produced by electric disintegration of metals, and, in particular, of platinum, as well as certain organic preparations—wood and nettle fibres, &c.—“metallized” by means of gold solution. He conjectured that he handled submicroscopic grating structures, although this could not be directly proved; he also assumed that grating polarization in the Hertzian sense first appeared with distances smaller than half the wave-length.

§ 4. The effect on Hertzian waves of an infinitely long metal cylinder was calculated by Dr. Seitz† for particular cases, in which, however,  $d/\lambda$  remained  $< 0.007$ .

Dr. v. Ignatowsky‡ applied himself to the same problem, and in addition, that of dielectric wires.

Prof. Schaefer and Dr. Grossmann§ investigated the diffraction of electromagnetic waves by dielectric (water-) cylinders theoretically as well as experimentally.

Prof. Schaefer and Dr. Reiche|| have quite lately contributed to the theory of grating inversion. The assumption that the thickness of the wire is very small compared with the wave-length, made in all the above theoretical contributions, is unavoidable in view of actual computation; in fact  $d/\lambda$  ought in no case to be greater than unity, and it is better for it to be less than one-half.

Stress must be once again laid on the fact that the phenomena here treated are only indirectly connected with polarization caused by diffraction; as we have repeatedly remarked, the greater the wave-length the more do wire gratings merge from diffracting appliances into pure polarizers. The polarization of diffracted light by glass gratings is comprehensively treated by Fröhlich¶, by whom many theoretical and experimental investigations of different experimenters, which are also of interest in connexion with our investigations, are described.

\* Ferd. Braun, *Ann. d. Phys.* xvi. pp. 1 & 238 (1905); *Physik. Zeitschr.* v. p. 199 (1904). See also O. Wiener, *Physik. Zeitschr.* v. p. 332 (1904).

† W. Seitz, *Ann. d. Phys.* xvi. p. 746 (1905), xix. p. 554 (1906).

‡ W. v. Ignatowsky, *Ann. d. Phys.* xviii. p. 495 (1905).

§ Cl. Schaefer and F. Grossmann, *Ann. d. Phys.* xxxi. p. 455 (1910).

|| Cl. Schaefer and F. Reiche, *Ann. d. Phys.* xxxii. p. 577 (1910).

¶ J. Fröhlich, *Polar. of refracted light*, Leipzig, 1907. See also B. Pogány, *Physik. Zeitschr.* xii. p. 279 (1911).

## II. EXPERIMENTAL ARRANGEMENT.

§ 5. Our present investigation comprises essentially the wave-length region from  $24\text{--}108\ \mu$ ; we have carried out our measurements for the fluorite and rocksalt Reststrahlen as well as for the long-waved rays of the Welsbach-mantle, isolated by means of quartz lenses\*. In addition we have made measurements on the exceptionally long-waved rays of mean wave-length  $314\ \mu$ , produced by a quartz-mercury lamp†. On account of the slight intensity, however, we could in this case investigate the grating only in its normal position. All these rays are by no means homogeneous; their energy distribution is, however, sufficiently well known, and their non-homogeneity in general plays no very great part.

The Reststrahlen of fluorite, if they are produced by a Welsbach mantle and separated out by reflexion at three fluorite surfaces, possess an average wave-length of  $25\cdot5\ \mu$ . The homogeneity is greatly increased by the introduction of a thin plate of sylvine in the path of the rays. The energy curve approaches symmetry and the mean wave-length is decreased to about  $24\ \mu$ . We have availed ourselves of this simple resource by introducing a plate of sylvine of  $1\cdot75\text{ mm.}$  thickness in the path of the rays, which served as a window for the air-tight bell of our radiomicrometer.

New experiments have shown that the Reststrahlen of rocksalt, as produced by the method here applied, consist of two bands, of which the first is situated at  $46\cdot9\ \mu$ , the other at  $53\cdot6\ \mu$ ‡; the mean wave-length is about  $52\ \mu$ . It is supposed in this case that the rays are transmitted through a quartz plate  $1\cdot2\text{ mm.}$  in thickness. This condition was approximately fulfilled, for the radiomicrometer window in our investigation consisted of a quartz plate  $1\text{ mm.}$  thick.

The energy of radiation in the case of the long-waved heat rays of  $108\ \mu$  isolated from the Welsbach mantle by means of quartz lenses was barely sufficient for measurements to be carried out with gratings normal to the path of the rays; in inclined positions, on the other hand, the thickness of the quartz layer within the path of rays had to be reduced from

\* H. Rubens and R. W. Wood, *Berl. Sitzungsber.* p. 1122 (1910).

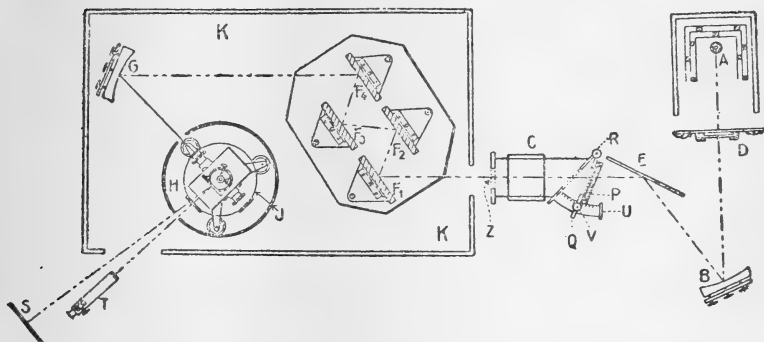
† H. Rubens and O. v. Baeyer, *Berl. Sitzungsber.* p. 339 (1911); *Phil. Mag.* [6] xxi. p. 689 (1911); *Verh. D. Phys. Ges.* xiii. p. 393 (1911). This non-homogeneous radiation, separated out by means of quartz lenses and filtered through black cardboard, consists principally of two parts, the mean wave-lengths of which are  $218\ \mu$  and  $343\ \mu$  respectively, of such a kind that the intensity of the long-waved portion is three times as much as that of the short-waved.

‡ H. Rubens and H. Hollnagel, *Berl. Sitzungsber.* 1910, p. 26.

17 to 13 mm. in order to increase the deflexions. Two series of experiments showed good agreement, and gave  $100\ \mu$  as the mean wave-length of the radiation. The non-homogeneity of the radiation was not much greater than that produced by introducing the thicker quartz plate.

§ 6. The experimental arrangement for Reststrahlen is shown in fig. 1. A denotes the Welsbach mantle, which serves as the radiating source, placed in a case closed on three sides; opposite the fourth side is arranged a movable rocksalt plate D, which serves as a trap-door. The rays fall

Fig. 1.



directly on the silver concave mirror B, then at the polarizing angle on the plane mirror E, consisting of selenium in the experiments on fluorite Reststrahlen, and quartz in those of rocksalt. Both substances are sufficiently transparent for the rays in question, and possess a very high index of refraction\*. They are particularly suitable, therefore, as reflecting polarizers.

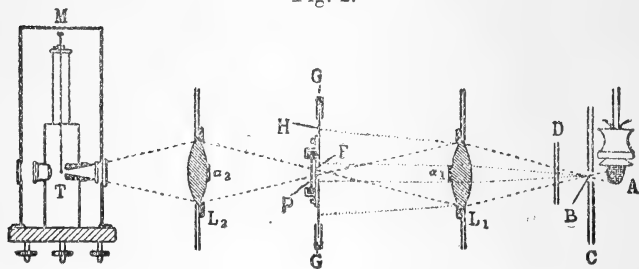
After the rays have been linearly polarized in the horizontal plane by reflexion at the mirror E, they pass through the wire grating P, which is mounted on a revolving support C. This support has already been completely described in our previous contribution (*l. c.* § 4). It consists of a horizontal brass tube, capable of orientation about its axis of revolution, cut at right angles at one end, and at an angle of  $44^{\circ}.4$  at the other. To this latter end a brass plate Q with a square opening is fixed, which can be orientated about

\* Selenium mirrors were first used as polarizers by A. Pfund, Johns Hopkins Univ. Circular, iv. p. 13 (1906). This element shows only a slight dispersion in the infra-red, for there its optical refractive index is equal to the square root of its dielectric constant. A selenium plate of 0.5 mm. thickness transmits 35 per cent. fluorite Reststrahlen. Quartz is still considerably more transparent for rocksalt Reststrahlen.

the axis R. The deviation between the brass plate and the axis of revolution of the tube can be read off by means of the circular scale U. V serves to make the plate fast in any required position. The investigated grating is fixed to the brass plate by means of clampscrews, in such a way that the wires of the grating remain exactly parallel to the axis of rotation R. The pencil of rays is bounded by a right-angled diaphragm, fixed to the back of the plate Q. Thus when the grating is moved the effective cross-section of the ray-pencil remains unchanged. This is necessary if the direct action of the rays is to be compared with that after transmission through the grating. A circular diaphragm of 25 mm. inner diameter is attached to the straight end of the tube.

The concave mirror B is so adjusted that an image of the source A is formed near the centre of the tube C. The rays afterwards pass into the box K, which contains the necessary reflecting surfaces for the production of the Reststrahlen\*, and after reflexion at these surfaces and at the concave mirror G reach the microradiometer H contained in an air-tight bell†. The polarization of the rays is very complete. This is to be expected from their small divergence, which in these experiments scarcely exceeded  $\pm 3^\circ$ .

Fig. 2.



§ 7. The experimental arrangement for the long waves is illustrated in fig. 2, and resembles in many important points

\* For the fluorite Reststrahlen three and for the rocksalt four reflecting surfaces were applied. By using the rocksalt screen the rays appeared to be very pure in both cases; at any rate the impurity was less than 1 per cent. The high purity of the rocksalt Reststrahlen is partly explained by the effect of the polarizing quartz plate, which, on account of its high refractive index for long waves, reflects these rays much better than the short-waved heat rays which can be transmitted through the quartz window.

† With respect to the construction and arrangement of the radiometer reference may be made to the following:—H. Schmidt, *Ann. d. Phys.* xxix. p. 1003 (1909); H. Rubens and H. Hollnagel, *Phil. Mag.* [6] xix. p. 764 (1910).



that used by Prof. Wood and one of us. The Invert-mantle A, the screen C with diaphragm B, the quartz lenses  $L_1$ ,  $L_2$  with mounted central screens  $\alpha_1$  and  $\alpha_2$ , the radiomicrometer M and the thin glass disk trap-door D are identical with those of the former arrangement. The screen with diaphragm F situated between the lenses  $L_1$  and  $L_2$  has, however, been altered as follows: a brass disk H with a circular diaphragm F\* is capable of motion in a circular groove G. The wire grating P can be attached securely to the plate H by means of clampscrews. Finally, the rotating support, denoted in fig. 1 by C, is placed between the lens  $L_1$  and the diaphragm F; to avoid complications this is omitted in fig. 2.

With regard to the details concerning the arrangement of the quartz lenses reference should be made to the papers already cited. It is only necessary to mention here that in taking advantage of the extraordinary difference in the indices of refraction of quartz for heat rays on both sides of the region of absorption (1.50 to 2.14), the diaphragms and lenses were so arranged that the rays of large wave-length emitted through the diaphragm B were united by means of the lens  $L_1$  at the diaphragm F, and later on concentrated on the microradiometer by means of the lens  $L_2$  (dashed lines). The ordinary short-waved heat rays, which form a divergent pencil behind the lens  $L_1$ , were held back partly by the plate H and partly by the central screen  $\alpha_1$  (dotted lines). By introducing a rocksalt plate 10 mm. thick in their path, it was proved that long-waved rays of approx. 100  $\mu$  were free of short-waved impurities.

§ 8. As polarizer we applied first of all quartz plates. We were soon convinced, however, that one of our finest metal wire gratings was a much more complete and convenient polarizer, the intensity being also stronger. For this reason the platinum grating Pt 1a was always kept fixed to the plate H and used as a polarizer. This convenient rotating polarizer was of very great advantage.

The observations were then carried out in such a way that by means of the rotating support C the investigated grating was inclined to the path of the rays, and a number of deflexions measured for two positions of the polarizer: 1, when the wires of the gratings were parallel, and 2, when they were at right angles to one another. The investigated grating was then removed and the deflexions again measured in both positions of the polarizer. These, on account of circumstances which are treated later on due to the fact that the

\* This should in fig. 2 be more to the right, at the point of section of the rays.

Auer-mantle itself emits partially polarized rays, were not equal.  $Q_s$  and  $Q_p$ , the transmissibility of polarized rays **II** and **I** to the wires, as well as the transmissibility ratio  $n^2 = Q_s/Q_p$ , could then be calculated corresponding to a given inclination to the wave-front.

§ 9. In our previous paper we gave an account of our investigations with eight wire gratings, which included very thin platinum, copper, iron, gold, and silver wires of French manufacture. Out of these eight we felt compelled for certain reasons to limit ourselves to five; the iron gratings had suffered too much damage in the meantime. One of them, however, in addition to the coarser platinum grating, served well for control investigations. In all these gratings the true slit-width  $b$  was exactly equal to the diameter of the wire  $d$ ; the true "grating constant," *i. e.* the periodic interval from one wire axis to the next, is  $a = 2b = 2d$ . If now the plane of the grating is inclined at an angle  $\beta$  to the wave-front in such a way that the wires remain parallel to the section of both planes, then the apparent grating constant  $a'$  is evidently given by  $a' = a \cos \beta$ , and the apparent aperture  $b'$  by

$$b' = d(2 \cos \beta - 1).$$

With the above-mentioned maximum inclination of the plate **Q** to the axis of the tube ( $44^\circ.4$ , fig. 1) we have

$$\cos 45^\circ.6 = \sin 44^\circ.4 = 0.700,$$

so that by fixing the finest grating ( $d = 25 \mu$ ) to that plate, the apparent slit-width was exactly  $10 \mu$ .

TABLE I.

$\beta$ .	$2 \cos \beta - 1$ .	Pt 1!		Cu 1!!		Au 1!!!		Ag 1!		Cu 2!	
		$a'$	$b'$	$a'$	$b'$	$a'$	$b'$	$a'$	$b'$	$a'$	$b'$
$0^\circ$	1.000	50.0	25.0	50.0	25.0	66.2	33.1	91.2	45.6	105.0	52.5
5	0.992	49.8	24.8	49.8	24.8	65.9	32.8	90.9	45.3	104.6	52.1
10	0.970	49.3	24.3	49.3	24.3	65.4	32.3	90.0	44.4	103.5	51.0
15	0.932	48.3	23.3	48.3	23.3	64.1	31.0	88.2	42.6	101.5	49.0
20	0.879	47.0	22.0	47.0	22.0	62.3	29.2	85.7	40.1	98.6	46.1
25	0.812	45.3	20.3	45.3	20.3	60.1	27.0	82.7	37.1	95.1	42.6
30	0.732	43.3	18.3	43.3	18.3	57.5	24.4	79.0	33.4	91.0	38.5
35	0.638	41.0	16.0	41.0	16.0	54.2	21.1	74.7	29.1	86.0	33.5
40	0.532	38.3	13.3	38.3	13.3	50.8	17.7	70.0	24.4	80.4	27.9
45	0.414	35.4	10.4	35.4	10.4	46.8	13.7	64.5	18.9	74.2	21.7
50	0.286	32.2	7.2	32.2	7.2	42.6	9.5	58.6	13.0	67.5	15.0
55	0.148	28.7	3.7	28.7	3.7	38.0	4.9	52.3	6.7	60.3	7.8
60	0	25.0	0	25.0	0	33.1	0	45.6	0	52.5	0

We give in Table I. the dimensions of the gratings

employed, ascertained by means of a dividing machine; their surfaces were rectangular in shape, of sides 20–30 mm. They were all previously optically investigated by means of a spectrometer and sodium light. The relative quality of the refracted image, which characterizes the uniformity of the grating and hence its structure, is further roughly indicated by the interposition of one or more exclamation marks (!) in Table I. In addition to the values of  $a$  and  $b$ , corresponding to  $\beta=0$ , we have calculated those of the apparent grating constants and slit-widths  $a'$ ,  $b'$  respectively for angles of inclination increasing by  $5^\circ$  from  $5^\circ$  to  $60^\circ$ , where  $b'$  finally disappears.

### III. TRANSMISSION THROUGH WIRE GRATINGS.

§ 10. We will describe the properties of our gratings in the same order as in the previous paper, from which Table II. is extracted besides forming a continuation of that table (*l. c.* § 12). At that time the wave-lengths were determined by measurements with a fluorite prism\*; later observations† proved them to be a little too large; the error is not considerable up to  $3\mu$ , scarcely more than 2 per cent.; for  $5\mu$ , however, it is about 10 per cent., so that we have now ascribed the proper value to the wave-length  $4.5\mu$ .

Table II. contains for each of the five gratings the ratio  $n^2$  of the transmissibility of polarized rays for  $\beta=0^\circ$  and  $45^\circ.6$ , beginning with a number of the previously investigated wave-lengths from  $0.49\mu$  (F line) to  $4.5\mu$ . Then follow those for fluorite Reststrahlen ( $24\mu$ ), rocksalt Reststrahlen ( $52\mu$ ), isolated rays through quartz lenses ( $100\mu$ ), the same after further filtration through a quartz plate 4 mm. thick ( $108\mu$ ), and, finally, the long waves of the quartz-mercury lamp (about  $314\mu$ ).

By referring to the table we see that the gratings—with one exception—polarize in the Hertzian sense after passing the neutral inversion point where  $Q_s=Q_p$  ( $n^2=1$ );  $n^2$  decreases more and more with increasing wave-length, in such a manner that it practically vanishes at  $100\mu$  when the grating is inclined at  $45^\circ.6$ , while with Pt 1 and Cu 1 the 1 transmission only amounts to 3 and 5 per cent. respectively. The purer and somewhat longer waves ( $108\mu$ ) become with these gratings up to 1 and 3 per cent. completely polarized. For the longest waves (about  $314\mu$ ), the polarization is in every case complete.

\* H. Rubens and W. Snow, *Wied. Ann.* xlv. p. 530 (1892); see *l. c.* Table I.

† H. Rubens, *Wied. Ann.* li. p. 381 (1894); F. Paschen, *Wied. Ann.* liii. p. 301 (1894).

TABLE II.

Grating .....	Pt 1.			Cu 1.			Au 1.			Ag 1.			Cu 2.		
	0°	45°-6	n <sup>2</sup>	0°	45°-6	n <sup>2</sup>	0°	45°-6	n <sup>2</sup>	0°	45°-6	n <sup>2</sup>	0°	45°-6	n <sup>2</sup>
$\beta$ .....	25.0	10.0		25.0	10.0		33.1	13.3		45.6	18.3		52.5	21.0	
$b'$ .....															
$\lambda$ .....	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>	n <sup>2</sup>
(F) 0.49 $\mu$ .....	1.036	1.110		1.017	1.049		1.014	1.033		1.019	1.044		1.010	1.025	
1.00 .....	1.06	1.16		1.14	1.41		1.10	1.31		1.11	1.22		...	...	
1.50 .....	1.03	1.07		1.14	1.40		1.09	1.29		1.05	1.13		1.04	1.13	
2.00 .....	0.99	0.98		1.13	1.35		1.05	1.13		1.01	1.01		...	...	
2.50 .....	0.97	0.92		1.10	1.21		1.02	1.06		0.97	0.94		...	...	
3.00 .....	0.94	0.85		1.04	1.07		0.99	...		0.96	0.91		...	...	
4.50 .....	0.80	0.51		0.90	0.52		0.89	0.73		0.89	0.78		0.92	0.84	
24 $\mu$ .....	0.68	0.13		0.73	0.16		0.51	0.11		0.61	0.20		0.86	0.31	
52 .....	0.37	0.08		0.41	0.14		1.05!	0.10		0.96	0.06		0.80	0.11	
100 .....	0.03	0.00		0.05	0.006		0.10	0.015		0.33	0.016		0.45	0.014	
108 .....	0.01	...		0.03	...		0.09	...		0.31	...		0.39	...	
ca. 314 .....	0.00	...		0.00	...		0.00	...		0.00	...		0.00	...	

§ 11. On account of the very weak intensity of the radiation we could not in our experiments upon Reststrahlen in 1904 carry out observations with inclined gratings. With our present arrangement and the increased sensitiveness of our measuring instruments we were now able to determine the transmissibility ratio as a function of the apparent slit-width. The results are collected together in the following tables and figures :—

For fluorite Reststrahlen ( $\lambda=24\mu$ ) : Table III. (p. 334) and fig. 3.

For rocksalt Reststrahlen ( $\lambda=52\mu$ ) : Table IV. (p. 335) and fig. 4.

For isolated long-waved rays ( $\lambda=100\mu$ ) : Table V. B and fig. 5 (pp. 336-337).

Fig. 3.

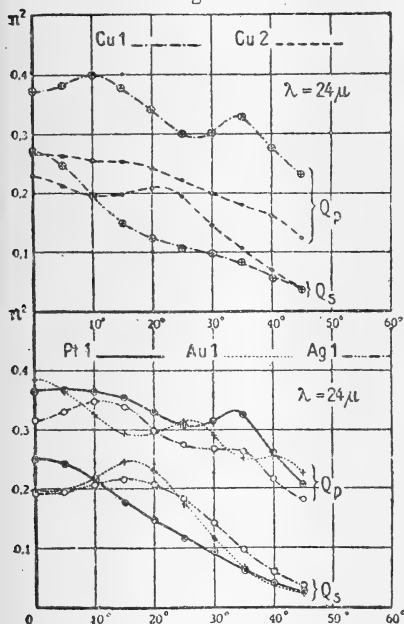
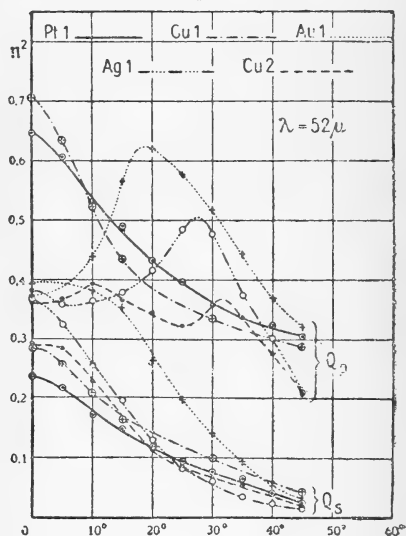


Fig. 4.



For the  $100\mu$  waves the directly observed apparent values  $Q_s'$  and  $Q_p'$  are cited in Table V. A (p. 337) ; these need correction because the analysing grating Pt 1a, in this case only, polarized up to 3 per cent. A simple recalculation gives the true values  $Q_s < Q_s'$  and  $Q_p > Q_p'$  in Table V. B.

A glance shows that the curves are much more complicated than our previous ones : we have therefore preferred to express  $Q_s$  and  $Q_p$  directly as empirical functions of  $\beta$ . The

TABLE III.

 $\lambda = 24 \mu$ .

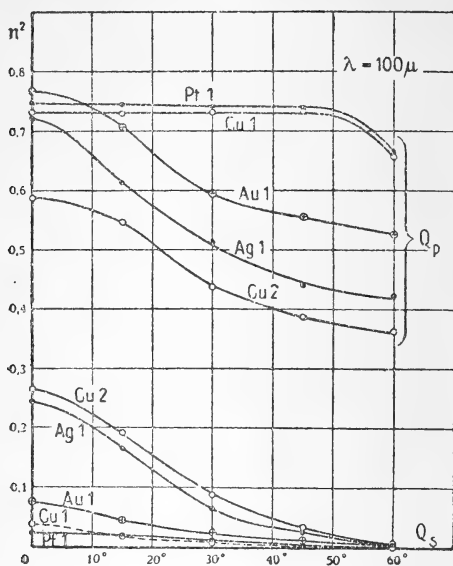
Grating:	Pt 1.			Cu 1.			Au 1.			Ag 1.			Cu 2.		
	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$
$\beta$ .															
0° ...	0.250	0.366	0.684	0.270	0.373	0.725	0.198	0.385	0.514	0.191	0.315	0.606	0.230	0.267	0.860
5 ...	0.240	0.367	0.654	0.247	0.382	0.644	0.199	0.363	0.548	0.195	0.330	0.591	0.213	0.262	0.815
10 ...	0.216	0.362	0.619	0.196	0.399	0.491	0.219	0.323	0.673	0.206	0.347	0.594	0.196	0.256	0.765
15 ...	0.177	0.352	0.503	0.147	0.374	0.393	0.242	0.292	0.829	0.215	0.338	0.636	0.199	0.252	0.790
20 ...	0.146	0.328	0.445	0.122	0.340	0.367	0.227	0.297	0.763	0.206	0.299	0.689	0.209	0.242	0.864
25 ...	0.117	0.309	0.377	0.106	0.300	0.352	0.174	0.314	0.555	0.181	0.274	0.661	0.194	0.221	0.878
30 ...	0.094	0.316	0.298	0.096	0.301	0.319	0.117	0.291	0.402	0.141	0.268	0.524	0.144	0.199	0.724
35 ...	0.060	0.327	0.185	0.081	0.330	0.245	0.065	0.250	0.261	0.096	0.262	0.364	0.105	0.179	0.586
40 ...	0.040	0.260	0.152	0.053	0.278	0.191	0.038	0.253	0.151	0.060	0.213	0.283	0.069	0.161	0.426
45 ...	0.027	0.204	0.130	0.037	0.230	0.159	0.025	0.222	0.111	0.037	0.180	0.207	0.039	0.121	0.322

TABLE IV.  
 $\lambda = 52 \mu$ .

Grating:			Cu 1.			Au 1.			Ag 1.			Cu 2.		
$\beta$ .	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$	$n^2$	$Q_s$	$Q_p$
0° ...	0.235	0.643	0.365	0.285	0.750	0.405	0.393	0.373	1.052	0.367	0.382	0.960	0.290	0.362
5 ...	0.216	0.604	0.358	0.257	0.635	0.405	...	...	...	0.325	0.359	0.910	0.286	0.367
10 ...	0.171	0.530	0.322	0.209	0.524	0.399	0.380	0.439	0.866	0.252	0.365	0.690	0.227	0.392
15 ...	0.149	0.490	0.304	0.162	0.438	0.370	0.352	0.565	0.624	0.195	0.379	0.515	0.167	0.362
20 ...	0.119	0.431	0.275	...	...	...	0.261	0.620	0.421	0.130	0.415	0.312	0.115	0.347
25 ...	0.090	0.398	0.226	...	...	...	0.126	0.576	0.341	0.080	0.484	0.165	0.088	0.322
30 ...	0.075	0.356	0.210	0.097	0.335	0.289	0.140	0.518	0.270	0.062	0.477	0.130	0.066	0.357
35 ...	0.066	0.339	0.193	...	...	...	0.104	0.442	0.235	0.034	0.373	0.091	0.056	0.337
40 ...	0.039	0.323	0.120	...	...	...	0.052	0.370	0.145	0.023	0.301	0.076	0.038	0.278
45 ..	0.026	0.304	0.081	0.042	0.290	0.145	0.034	0.320	0.106	0.012	0.208	0.058	0.023	0.203

choosing of  $b'$  as single independent variable appeared, with our previous conditions of experiment, to be valid; more variables must, however, at present be taken into account.

Fig. 5.



This also explains, among other things, why previously a small inclination of the grating had scarcely any significance, while now for values of  $\beta = \pm 5^\circ$  considerable differences appear in some cases in comparison with the normal position  $\beta = 0^\circ$ .

§ 12. Four types of curves may be distinguished:—

*Type I.* (Cu 2, Ag 1, Au 1, at  $24\mu$ ):  $Q_s$  shows one maximum,  $Q_p$  two. In the case of Cu 2 the maxima certainly appear only feebly indicated.

*Type II.* (Cu 1, Pt 1, at  $24\mu$ ; Cu 2 at  $52\mu$ ):  $Q_s$  falls off gradually,  $Q_p$  shows two maxima.

*Type III.* (Ag 1, Au 1, at  $52\mu$ ):  $Q_s$  decreases gradually,  $Q_p$  exhibits one well pronounced maximum. It is to be remarked that Au 1 polarizes  $\perp$  with an uninclined grating, while at about  $5^\circ$  a point of inversion exists and  $\parallel$  polarization in the Hertzian sense first appears at larger inclinations; this behaviour was checked several times. It has already been remarked that the grating is made up of gilded silver wire.



TABLE V.—A ( $\lambda=100 \mu$ ).

Grating .....	Pt 1.		Cu 1.		Au 1.		Ag 1.		Cu 2.	
	$Q_s'$	$Q_p'$	$Q_s'$	$Q_p'$	$Q_s'$	$Q_p'$	$Q_s'$	$Q_p'$	$Q_s'$	$Q_p'$
$\beta$ .										
0° .....	0.043	0.727	0.058	0.713	0.095	0.746	0.255	0.708	0.272	0.578
15 .....	0.039	0.722	0.038	0.709	0.064	0.689	0.178	0.599	0.201	0.534
30 .....	0.034	0.718	0.029	0.713	0.040	0.577	0.074	0.498	0.099	0.427
45 .....	0.024	0.720	0.024	0.711	0.026	0.540	0.034	0.427	0.045	0.379
60 .....	0.019	0.645	0.022	0.631	0.023	0.512	0.019	0.415	0.015	0.352

B ( $\lambda=100 \mu$ ).

Grating:	Pt 1.		Cu 1.		Au 1.		Ag 1.		Cu 2.	
	$Q_s$	$Q_p$	$Q_s$	$Q_p$	$Q_s$	$Q_p$	$Q_s$	$Q_p$	$Q_s$	$Q_p$
$\beta$ .										
0° ...	0.022	0.748	0.038	0.731	0.075	0.766	0.241	0.722	0.263	0.587
15 ...	0.018	0.743	0.018	0.729	0.045	0.708	0.165	0.612	0.191	0.544
30 ...	0.013	0.739	0.008	0.734	0.024	0.593	0.061	0.511	0.089	0.437
45 ...	0.003	0.740	0.004	0.732	0.011	0.555	0.022	0.439	0.035	0.389
60 ...	0.000	0.654	0.004	0.649	0.003	0.527	0.007	0.427	0.005	0.362
			$n^2$	$n^2$	$n^2$	$n^2$	$n^2$	$n^2$	$n^2$	$n^2$
0° ...	0.000	0.000	0.000	0.006	0.005	0.015	0.050	0.016	0.000	0.014
15 ...	0.003	0.004	0.004	0.011	0.005	0.020	0.022	0.039	0.035	0.090
30 ...	0.008	0.018	0.008	0.011	0.004	0.041	0.061	0.119	0.089	0.204
45 ...	0.018	0.024	0.018	0.025	0.005	0.063	0.165	0.269	0.191	0.351
60 ...	0.038	0.038	0.038	0.054	0.003	0.093	0.241	0.334	0.263	0.447

C ( $\lambda=314 \mu$ ).

Grating:	Pt 1.		Cu 1.		Au 1.		Ag 1.		Cu 2.	
	$Q_s$	$Q_p$	$Q_s$	$Q_p$	$Q_s$	$Q_p$	$Q_s$	$Q_p$	$Q_s$	$Q_p$
$\beta$ .										
0° ...	0.000	0.923	0.000	0.930	0.000	0.850	0.000	0.790	0.000	0.780

*Type IV.* (Cu 1, Pt 1, at  $52\mu$ ; all the curves for  $100\mu$ ):  $Q_s$  and  $Q_p$  both decrease uniformly as the inclination of the grating increases. In addition it is noticed that, up to an inclination of a little over  $45^\circ$ , both Cu 1 and Pt 1 show a practically constant  $Q_p$ , of nearly the same value, at  $100\mu$ .

TABLE VI.

$$\beta = 0^\circ.$$

Grating.	$d$ .	$a$ .	$\lambda$ .	$a/\lambda$ .	Type.
Cu 2.....	52.5	105.0	$24\mu$	4.36	} I.
Ag 1.....	45.6	91.2	"	3.80	
Au 1.....	33.1	66.2	"	2.76	
Cu 1.....	25.0	50.0	"	2.08	} II.
Pt 1.....	25.0	50.0	"	2.08	
Cu 2.....	52.5	105.0	$52\mu$	2.02	} III.
Ag 1.....	45.6	91.2	"	1.76	
Au 1.....	33.1	66.2	"	1.27	
Cu 1.....	25.0	50.0	"	0.96	
Pt 1.....	25.0	50.0	"	0.96	
Cu 2.....	52.5	105.0	$100\mu$	1.05	} IV.
Ag 1.....	45.6	91.2	"	0.91	
Au 1.....	33.1	66.2	"	0.66	
Cu 1.....	25.0	50.0	"	0.50	
Pt 1.....	25.0	50.0	"	0.50	

A study of Table VI., in which the order of the gratings for each wave-length is inverted in comparison with the previous tables, may simplify our view of these complications. It contains the ratios of the grating constants to the *mean* wave-length of our non-homogeneous radiation; these decrease more and more, and the gratings now arrange themselves according to the above types. So far as the elementary equation of diffraction

$$\sin \gamma = m \cdot \frac{\lambda}{a}$$

may be considered applicable, the angle of diffraction  $\gamma$  does not become imaginary for integral values of  $m \leq a/\lambda$ . The digit before the decimal point in the above table consequently gives, when the grating is perpendicularly fixed, the number of diffracted images on each side of the principal image

which can appear when the grating is inclined. In this sense corresponds

Type I. to two or more diffracted images.

Type II. to two diffracted images.

Type III. to one diffracted image.

Type IV. to no diffracted image.

§ 13. In the arrangement for the waves of  $100\mu$  wavelength, the inclination of the grating could be increased even up to  $60^\circ$ , whereby  $b' = 0$  finally, so that any grating ceases to be transparent for light waves at this angle. In fact the corrected  $Q_s$  disappear with the exception of a few permilles, which are probably due to slight irregularities. The Hertzian polarization is, accordingly, as good as complete. It is remarkable that the values of  $Q_p$  remain quite considerable.

In addition the values of  $Q_s$  at  $24\mu$  and  $52\mu$  seem to converge towards zero in such a way that, conjecturally, they would vanish at  $60^\circ$ ; our rotating support (see fig. 1) did not, however, allow a greater inclination than  $45^\circ.6$ .

The gratings Pt 1 and Cu 1—the only two possessing equal diameters of wire—behave almost similarly throughout. It is difficult to tell whether the slight divergence between the two is due to difference of material or of geometrical configuration.

In the previous investigation with two copper gratings Cu 1 and Cu 2 of different wire diameters, it was shown that the transmissibility ratio depended only on the apparent width of aperture, and not perceptibly on the radius of curvature of both the contiguous metal wires. Table VII.

TABLE VII.

Grating.	$\beta$ .	$b'$ .	$n^2$ .				
			$1.5\mu$ .	$4.5\mu$ .	$24\mu$ .	$52\mu$ .	$100\mu$ .
Cu 2...	$0^\circ$	$52.5\mu$	1.04	0.92	0.86	0.80	0.45
	30	38.5	1.05	0.91	0.72	0.19	0.20
	40	27.9	1.09	0.87	0.43	0.14	...
	45	21.7	1.13	0.84	0.32	0.11	0.09
	60	0	...	...	...	...	0.01
Cu 1...	$0^\circ$	$25.0\mu$	1.13	0.87	0.73	0.41	0.05
	15	23.3	...	...	0.39	0.37	0.025
	30	18.3	1.17	0.82	0.32	0.29	0.010
	45	10.4	1.41	0.59	0.14	0.15	0.005
	60	0	...	...	...	...	0.006

is similar throughout to our previous table viii. ; while, however, the borrowed columns for  $1.5$  and  $4.5 \mu$  approximately prove the correctness of the above assertion, they entirely fail to do so for the longer wave-lengths.

On the whole the values here for  $n^2$  at a given slit-width  $b'$ , in case of the finer grating Cu 1, are perceptibly larger than those of the coarser Cu 2, so that, in the Hertzian sense, the latter *cet. par.* polarizes more completely.

§ 14. The coarser platinum grating Pt 2 ( $b=48 \mu$ ) fixed normally gave, approximately,  $n^2=0.35$  at  $108 \mu$ , being already a considerable though incomplete polarization.

The iron grating Fe 1, which was by no means perfect even in 1893, has in the meantime, through rust, been completely spoiled, so that exact measurements were impossible; this, however, also showed a strong Hertzian polarization, which at  $108 \mu$  is represented by a value of  $n^2=0.15$ .

We finally investigated a very coarse silver grating ( $a=372 \mu$ ,  $b=186 \mu$ ), which, by means of sulphuretted hydrogen, was nearly completely blackened; this gave the following values for the long-waved radiations (about  $314 \mu$ ) of the quartz-mercury lamp :—

$$\begin{array}{l|l} Q_s=0.30 & Q_m=0.435 \\ Q_p=0.57 & n^2=0.53, \end{array}$$

which are of the same order of magnitude as those given by the copper grating Cu 2, which is about  $3.5$  times finer, at  $\lambda=100 \mu$  (Table V. B).

We previously mentioned (*l. c.* § 19) that a glass-fibre grating shows an exceptionally small effect in the visible spectrum. We have, in our present contribution, abstained from testing regular dielectric gratings.

We have, on the other hand, tested a grating-like Auer mantle with respect to its transmissibility (see § 16 below), and found that in the Hertzian sense it polarizes with an approximate value of  $n^2=0.55$  at  $\lambda=100 \mu$ . The material, as is known, consists of a solid solution of 1 per cent. cerium oxide in thorium oxide, and may indeed be considered, at least at white heat, as a conductor.

#### IV. REFLEXION AND EMISSION.

§ 15. To determine the reflecting power of the silver grating Ag 1 we carried out the following series of experiments. The rays of the Invert mantle A were first of all reflected by a plane silver surface at  $45^\circ$ ; it was here assumed that no loss occurred; the reflected rays fell on the

aperture B in the screen C; the rest of the arrangement was identical with that depicted in fig. 2 for rays of wavelength  $100\ \mu$ .

The deflexions were determined for vertical and horizontal directions of the wires of the platinum grating Pt 1, which, as before, acted as analyser; on account of the polarized emission of the Auer mantle, to be referred to below, a certain difference between the two deflexions was noticeable.

The silver grating Ag 1 was next placed—with wires vertical—so that its front surface was exactly in the same position as the above-mentioned silver surface, and the deflexions again measured. From these the reflecting powers  $R_s$  and  $R_p$  of polarized radiations normal and parallel to the wires, respectively, could be easily calculated; after correcting for the somewhat incomplete polarization of the platinum grating, they gave the following values:—

$$\begin{array}{ccc|ccc} R_s = 0.766 & & Q_s = 0.022 & & R_s + Q_s = 0.79 \\ R_p = 0.301 & & Q_p = 0.439 & & R_p + Q_p = 0.74 \end{array}$$

in which the values for  $Q_s$  and  $Q_p$  at  $45^\circ$  for Ag 1 are taken from Table V. B.

It is thus seen that the sum of the reflecting and transmitting powers is somewhat different in the two cases and less than unity. Regular diffraction will hardly occur here, while  $\lambda = 100\ \mu$ ,  $a = 91.2\ \mu$ ,  $a' = 64.4\ \mu$ ; a perceptible diffusion will, however, take place.

§ 16. A polarized temperature radiation of the gratings is, as a matter of course, very probable: we could not, however, apply white heat to such costly and sensitive appliances.

Some success was obtained in this respect with a specially woven grating-like Auer mantle, which exhibited a broad zone of exclusively vertically stretched threads: its emission was partially polarized. The radiation polarized  $\parallel$  to the threads amounted at  $100\ \mu$  to about 0.60 of that polarized at right angles. Unpolarized radiation was sent out by the glowing magnesia mantle-holder which is superposed on that observed; on correcting for this, the above fraction would become still smaller and eventually approximate to the value given above,  $n^2 = 0.55$ , which the same mantle acting as a grating gave for the transmissibility ratio. The above ratio at  $52\ \mu$  was, on the other hand, only of the order 0.95. A quantitative comparison can, however, scarcely come into consideration with such undefined structures; their properties at white heat would also no doubt differ from those at ordinary temperature.

## V. CONCLUSION.

§ 17. We were already led by our first investigations to the opinion that the further one was able to penetrate into the infra-red, the simpler the relations would become. While we had to limit ourselves in 1893 to the region

$$2 < b'/\lambda < 75,$$

the results in the present communication cover the interval

$$0.08 < b'/\lambda < 2;$$

if we consider the measurements for  $\lambda = 100 \mu$  carried out with an angle of inclination  $\beta = 60^\circ$ ,  $b'/\lambda$  even becomes equal to zero.

The problem which we set ourselves in the beginning may therefore be considered as solved. Indeed, the general result throughout corresponds to expectation, in that a practically complete Hertzian polarization finally occurred with all gratings (§ 10).

Our final result, which assumes quite a simple form, is throughout in unison with the principles of the electromagnetic theory of radiation. The special theories mentioned in the introduction also show the same final result, provided that  $b/\lambda$  or  $d/\lambda$  be only sufficiently small. The theories are still unsatisfactory with regard to the extended interval between; the relations there are much more complicated even, although they again simplify themselves in the first-mentioned optical region.

We are much indebted to Mr. Morris Owen for help in preparing this paper.

XXXIII. *Some New Mechanical Quadratures.*

By GEORGE F. BECKER\*.

**M**ECHANICAL quadratures are in some circumstances unavoidable, but they are usually shunned as clumsy and troublesome. Were the formulæ neater and their applicability better defined, they might be of great use in experimental physics and might compete with other integrations by series in the computation of functions. This paper is intended as a contribution to that end.

There are three distinct systems of mechanical quadrature, each depending upon the integration of a general formula for interpolation. By integrating Newton's interpolation formula, Simpson's rule, Weddle's rule and some others can

\* Communicated by the Author.

be found. These depend upon the assumptions that the increments of the abscissa are constant and that the differences above a certain order are negligible. It is said that if the attempt is made to include in quadratures of this species differences above the sixth, the formulæ become unmanageable, but this I have not tested. It is possible to base quadratures on Stirling's and Bessel's interpolation formulas, but as these are not applicable at the beginning or the end of a series of values their usefulness is limited, and since these modes of interpolation are founded on Newton's, the quadratures are not essentially different.

Gauss used as the basis of his method of quadratures Lagrange's interpolation formula. When after integration the increment of the abscissa is assumed to be constant, Cotes's numbers result, but Gauss showed that, by a proper selection of unequal increments of the independent variable, formulæ can be deduced whose convergence is very rapid. Unfortunately most of the increments are surds, rendering the application of the method very laborious in spite of its elegance.

Interpolation by means of Taylor's series has several advantages over methods depending upon finite differences, and its limitation to continuous functions is rarely of any moment. In dealing with known functions, the methods of infinitesimal calculus are habitually employed excepting for interpolation, while finite differences constitute a distinct algorithm. Since Taylor's series is the very foundation of analysis, its application to interpolation is both more consistent and more elegant than that of finite differences, while, if needful, the final results can be expressed in terms of finite differences without the least trouble. Similarly, so-called mechanical quadratures founded on Taylor's series in its application to interpolation are quadratures obtained by integration of a differential equation, and thus do not differ essentially from integrations by series. The expressions for quadrature to which Taylor's theorem leads are in some cases semi-convergent series, yet the error involved may be reduced *ad libitum*. Although convergent series would yield results of absolute accuracy were an infinite number of terms to be computed, this accuracy is purely theoretical and computation terminates when the error becomes negligible. The distinction between convergent and semi-convergent series is clear, yet there is no difference between the results obtainable by their use in effecting quadratures.

The quadrature founded on Taylor's series was first given

by Euler in 1732-3, but his paper was not printed until 1738. It was discovered independently by Maclaurin, who published it in 1742 \*. The very essential discussion of the remainder was left to Poisson, Jacobi and others. The formula for mechanical quadratures commonly given in textbooks, and ordinarily ascribed to Laplace, is merely Euler's equation with the substitution of finite differences for derivatives.

It is easy so to transform Taylor's series as to express an integral in terms of a sum of the ordinates and sums of the successive derivatives. The function to be integrated and its derivatives can be similarly expressed. From the system of equations thus developed, the sums of the derivatives can be eliminated and the result taken between limits is a definite integral expressed in terms of the sum of the ordinates, together with the derivatives at the limits. This is Euler's quadrature.

Let  $h$  be the constant increment of  $x$  and  $B_1, B_3, B_5 \dots$  be Bernoulli's numbers; for brevity let also

$$v = f^{(k)}(x_n) - f^{(k)}(x_0),$$

or the difference of the  $k$ th derivative at the two limits.

Then Euler's equation may be written thus :

$$\int_{x_0}^{x_n} y dx = h \left( \frac{y_0}{2} + y_1 + y_2 + \dots + \frac{y_n}{2} \right) - \frac{B_1 h^2 v'}{2!} + \frac{B_3 h^4 v'''}{4!} - \dots + R.$$

Of course

$$h = \frac{x_n - x_0}{n}$$

and  $h$  may be any integral factor of  $x_n - x_0$ . The total number of ordinates is  $n+1$  and they divide the area to be integrated into  $n$  parts each of width  $h$ .

Euler's formula is capable of some transformations which do not seem to have been noticed and a variety of special forms can be deduced from it. For this purpose it is convenient to make certain changes in notation. The first term of the second member is a polygon bounded by the axis, the extreme ordinates and chords connecting the extremities of all the ordinates. Let this polygon of chords be denoted by

\* Euler's formula, based on Taylor's theorem, will be found in *Commentarii Acad. Sci. Imp. Petrop.* vol. vi. ad annos 1732 et 1733; 1738, page 68; Maclaurin gives it in his 'Treatise of Fluxions,' 1742, page 672.



$C_1$  and let

$$C_2 = 2h \left( \frac{y_0}{2} + y_2 + y_4 + \dots + \frac{y_n}{2} \right)$$

$$\dots = \dots$$

$$C_m = mh \left( \frac{y_0}{2} + y_m + y_{2m} + \dots + \frac{y_n}{2} \right),$$

in which case  $n$  must be divisible by  $m$ . Evidently these are also polygons of chords and there is an Eulerian equation corresponding to each of them, obtainable by merely substituting  $mh$  for  $h$ . Let also

$$T = 2h(y_1 + y_3 + y_5 \dots + y_{n-1}) = 2C_1 - C_2.$$

Here  $T$  may be a polygon of tangents or of tangents with portions of the ordinates. It consists of  $n/2$  portions each of width  $2h$ . In any case the integral sought will be an area intermediate between  $T$  and  $C_m$  irrespective of the particular value of  $m$ . It is evident from the identity  $T \equiv 2C_1 - C_2$  that

$$\int_{x_0}^{x_n} y dx = T + (2^2 - 2) \frac{B_1 h^2 v'}{2!} - (2^4 - 2) \frac{B_3 h^4 v'''}{4!} + \dots + R.$$

Suppose  $n$ , or the number of strips into which the area is divided, to be a multiple of two. Then the integral is expressible by each of two or more Eulerian equations. If each of these is multiplied by an arbitrary multiplier and if the sum of these multipliers is unity, the sum of the equations will be a new expression for the integral. Furthermore, for every polygon of chords involved it will be possible to eliminate the coefficient of one difference of derivatives, or  $v$ . Thus if  $n=4$  the integral may be expressed in terms of  $T$ ,  $C_2$ , or  $C_4$ . Multiplying by arbitrary coefficients and adding the three equations makes it possible to impose three conditions: viz., that the sum of the multipliers shall be unity and that the coefficients of  $v'$  and  $v'''$  shall disappear. This transformation leaves the integral expressed in terms of the three polygons and of derivatives of the fifth and higher orders for which finite differences may be substituted if necessary.

So far as mere elimination is concerned there appears to be no limit to this process. Thus if  $x_n - x_0$  were to be divided into 60 parts, eleven coefficients could be eliminated and the integral would be expressed in terms of  $T$  and eleven polygons of chords, only the 23rd and higher derivatives or

differences appearing in the remaining portion of the series. For certain classes of functions this might be advantageous, but on account of the semi-convergence of Euler's series the desirable limit will in many instances be lower.

I have carried out the process only as far as  $n=12$ , which permits of the elimination of all the derivatives below the eleventh. The equations themselves show the appropriate factors, while the coefficient of the one derivative term retained is the sum of the coefficients in the several Euler series each multiplied by one of these factors. The following six formulas are thus obtained:—

$$\begin{aligned}
 (1) \quad \int_{x_0}^{x_n} y dx &= \frac{2T + C_2}{3} - 2h \frac{h^3 v'''}{360} + \dots & (n \geq 2) \\
 (2) \quad &= \frac{32T + 12C_2 + C_4}{45} - 4h \frac{h^5 v^{(5)}}{1890} + \dots & (n \geq 4) \\
 (3) \quad &= \frac{648T + 81C_2 + 112C_4 - C_6}{840} - 6h \frac{h^7 v^{(7)}}{5,600} + \dots & (n \geq 6) \\
 (4) \quad &= \frac{2,048T + 704C_2 + 84C_4 - C_8}{2,835} - 8h \frac{2h^7 v^{(7)}}{4,725} + \dots & (n \geq 8) \\
 (5) \quad &= \frac{35,000T + 14,375C_2 + 528C_4 - 7C_6}{49,896} - 10h \frac{10h^7 v^{(7)}}{12,096} & (n \geq 10) \\
 (6) \quad &= \frac{1,492,992T - 174,960C_2 + 585,728C_4}{1,801,800} \\
 &\quad - \frac{104,247C_4 + 2,288C_6 - C_{12}}{1,801,800} - 12h \frac{691h^{11} v^{(11)}}{750,750} + \dots & (n \geq 12)
 \end{aligned}$$

The derivatives in the last or corrective terms of these equations may be expressed in terms of finite differences should the latter be more convenient. The transformation is well known, but its most essential features may be noted here to save a reference. The  $k$ th derivative of a function,  $f^{(k)}(x)$ , multiplied by the  $k$ th power of the constant increment of  $x$ , here denoted by  $h$ , is expressible in terms of the  $k$ th finite difference and differences higher than the  $k$ th. For the purpose in hand Newtonian differences should be employed, because they are applicable at the beginning and at the end of a series of values. When the derivatives and differences are so large that higher derivatives and differences also require consideration the transformation is somewhat complex, but if the  $k$ th difference is technically "small"

so that the  $(k+1)$ st difference is negligible, then

$$h^k f^{(k)}(x) = \Delta^{(k)}$$

where  $\Delta$  denotes finite difference. In the formulæ  $v$  is employed to indicate the difference of the derivatives at the limits of the area to be integrated,  $x_0$  and  $x_n$ . Using a corresponding notation for the finite differences and assuming that the  $(k+1)$ st difference is inconsiderable

$$h^k v^k = \Delta_n^{(k)} - \Delta_0^{(k)}$$

and this substitution may be made in the corrective terms of the formulæ\*.

Not all of these equations are wholly new. The first term of (1) is only Simpson's rule in a new notation and if  $n$  is limited to 2 it is also identical with Cotes's rule for  $n=2$ . Omitting the derivatives, equations (2) and (3) also coincide with Cotes's rules for  $n=4$  and  $n=6$ , but if in these equations  $n$  is taken at any multiple of 4 and 6 numbers quite distinct from Cotes's result. All of the equations can be expressed in the same form as Cotes's, but this mode of statement seems undesirable because it masks the vital fact that a reduction of the value of  $h$  increases the accuracy of the result. Now no one would think of getting a considerable quadrature by Simpson's rule with the minimum value of  $n=2$ , because this rule with  $n=10$  gives a result the error of which approaches a 625th of that incurred by taking  $n$  at 2, while if in (6)  $n$  is taken at 24 instead of 12 the error is reduced approximately to 1/4096 of its maximum value.

So far as I know, equations (4), (5), and (6) are new, and Cotes's numbers for  $n=8$  and 10 do not fit into the system of quadratures here discussed.

The derivative term in each of the six equations may exceed the value of the remainder. If the difference of derivatives in this term is denoted by  $v^r$ , this is to be regarded as the definite integral of  $f^{(r+1)}(x)$  which, like any other function of real variables to be integrated, must preserve the same sign between the limits of integration. If the sign does not change and if also (as Poisson and Jacobi showed) the  $(r+1)$ st derivative does not pass through a maximum between the limits, then the final term of the equations exceeds in absolute value the remainder of the series. In

\* A discussion of the relations subsisting between derivatives and finite differences may be found in Smithsonian Math. Tables, 1908, page xxxvi, or elsewhere.

any case whatever let  $\lambda$  be the maximum value of  $f^{(r+1)}(x)$  between the limits, then the total area represented by the definite integral,  $v^r$ , must be less than  $\lambda(x_n - x_0)$ , and this substituted for  $v^r$  in the corrective term gives a quantity greater than the remainder of the Eulerian series. It is usually practicable so to select or subdivide the limits of integration that the  $(r+1)$ st derivative neither changes sign nor passes through a maximum, and then the corrective term of the equations approximately defines the error of the quadrature.

It is possible still further to reduce the limits of the remainder provided that certain assumptions are made with respect to succeeding differential coefficients, but this proviso implies an inquiry which in most instances would be laborious, more so than the division of  $h$  into two or more parts\*.

It will be observed that even in (6) the coefficients are numbers of manageable magnitude not exceeding 7 places. If the attempt were made to eliminate a larger number of derivative terms it is not improbable that the formulæ could be dealt with only by 10-place logarithms or computing machines.

The most accurate of the equations given above involves the division of  $x_n - x_0$  into some multiple of 12 parts.

Such a division may be inconvenient, for example in dealing with a function which is already tabulated to a decimal argument. This difficulty, however, may be avoided with little trouble; for, if 100 values of  $y$  are available, the quadrature from the first to the 96th may be effected by equation (6) and that of the remaining 4 items by equation (2). When experimental data are to be dealt with observations can usually be so arranged as to fit a duodecimal formula, and when time is the independent variable duodecimal division is of course most convenient.

In dealing with some functions one or two derivatives are readily calculated, or are perhaps already tabulated, while the higher derivatives are troublesome. It is worth while to observe, therefore, that it is as easy to eliminate the coefficients of the higher derivatives as of the lower ones, and that a formula similar to (6) could be found in which  $v'$  and  $v'''$  should be retained but  $v^{xi}$  and  $v^{xiii}$  cancelled.

\* The remainders in formulæ (1) to (6) arise from the remainders in the system of Taylor's series on which Euler's equation is based, and the published discussions of the remainder in Taylor's series would make a stout volume. No elaborate consideration of this subject seems needful for the purpose of this paper.

Odd values of  $n$  lend themselves less readily than even ones to the elimination of derivatives from Euler's series because of their limited divisibility. If  $n=3$  the quadrature may be written

$$\int_{x_0}^{x_n} y dx = \frac{9 C_1 - C_3}{8} - 3 h \frac{h^3 v'''}{240},$$

and the first term of this formula was given by Newton\*.

Comparison with (1) shows that it is somewhat less accurate than Simpson's rule. Newton's rule is derivable also from the integration of his interpolation formula, and if  $3h$  is taken as unity it coincides with Cotes's rule for  $n=3$ . The lowest odd number with two divisors is 9, so that with  $n=9$  two derivatives could be eliminated, but such a formula would be of small value.

It is noteworthy that the simpler rules for quadrature are derivable from any one of the three fundamental interpolation formulæ.

Other formulæ could be obtained by eliminating fewer coefficients than the divisibility of  $n$  permits. In general that would be a waste of opportunities, but two examples are worth noting. With  $n=6$  I find from T,  $C_2$ , and  $C_3$

$$\int_{x_0}^{x_n} y dx = \frac{15 T + 3 C_2 + 2 C_3}{20} - 6 h \frac{h^5 v^v}{5040} + \dots$$

which is Weddle's rule with a corrective term. Under normal circumstances it is considerably less accurate than (3), as can easily be shown by applying each of the equations to the same portion of the exponential curve.

Curiously compact and accurate is a formula derived from T,  $C_2$ ,  $C_3$ , and  $C_4$  in which the coefficient of  $C_2$  turns out to be zero. Of course  $n$  must be 12 or a multiple thereof. It may be written

$$\int_{x_0}^{x_n} y dx = \frac{1}{5} \left( 4 T + \frac{8 C_3 - C_4}{7} \right) - 12 h \frac{h^7 v^{vii}}{25,200} + \dots \quad (7)$$

Here the denominator of the corrective term is remarkably large or the remainder very small so that (7) may approach (6) in accuracy. Its simplicity makes it convenient for laboratory use. Economy of labour depends to some extent on the arrangement of computation, and for that reason I

\* *Opuscula, Methodus differentialis*, prop. vi, Scholium.

give in a footnote \* below the details of the quadrature by (7) of a portion of the ascending exponential. It will enable the reader to perceive that no advantage is obtained by stating the formulæ in terms of the ordinates instead of the polygons, even when the division of the area to be integrated is limited to the minimum value of  $n$ .

It is needless to say that the integrals (1) to (6) without the corrective terms are rigorous for finite series with  $n+1$  constants whose highest terms contain  $x^n$ . In any other case two distinct means exist for reducing the error of the result below a given tolerance, viz., a proper choice of the number of derivatives to be eliminated and a subsequent reduction of  $h$  so far as this may be needful. Even if Euler's series ultimately becomes divergent for a given function or class of functions, the earlier part of the series is convergent and there is some term after the first at which divergence begins; in other words, the best result for a given value of  $h$  is attainable by integrating a certain number

\* Find  $\int_{-1}^{+2.6} e^x dx$  with  $n=12$ , or  $h=0.3$ , taking values of  $y$  from Smithsonian Math. Tables, by (7).

$x.$	$y.$	T.	$C_3.$	$C_4.$
$x_0 = -1.0$	$y_0/2$		0.183 9397	0.183 9397
$x_1 = -0.7$	$y_1$	0.496 5853		
$x_2 = -0.4$	$y_2$		0.904 8374	
$x_3 = -0.1$	$y_3$	0.904 8374		1.221 403
$x_4 = +0.2$	$y_4$			
$x_5 = 0.5$	$y_5$	1.648 721		
$x_6 = 0.8$	$y_6$		2.225 541	
$x_7 = 1.1$	$y_7$	3.004 166		
$x_8 = 1.4$	$y_8$			4.055 200
$x_9 = 1.7$	$y_9$	5.473 947	5.473 947	
$x_{10} = 2.0$	$y_{10}$			
$x_{11} = 2.3$	$y_{11}$	9.974 182		
$x_{12} = 2.6$	$y_{12}/2$		6.731 869	6.731 869
$\Sigma$ .....		21.502 439	15.520 134	12.192 412
Factor .....		$2h$	$3h$	$4h$
Product .....		12.901 4634	13.968 1206	14.630 8944
		=T	= $C_3$	= $C_4$

These values substituted in (7) give for the answer 13.095 858. The true value of the last figure is 9.

For  $n=12$ , but not for any multiple of 12, (7) can be written

$$\int_{x_0}^{x_n} y dx = \frac{h}{5} \left\{ \frac{10}{7} (y_0 + y_{12}) + 8(y_1 + y_5 + y_7 + y_{11}) + \frac{80}{7} (y_3 + y_9) \right. \\ \left. + \frac{24}{7} y_6 - \frac{4}{7} (y_4 + y_8) \right\}.$$

[No arithmetical work is saved by adopting this method of statement.]

of terms of Euler's series. This amounts to a choice between formulæ (1) to (6) or others similarly derived. Thereafter the only question is how small a value of  $h$  must be adopted to give the required accuracy. Any quadrature by series assumes a fictitious curve more or less nearly coinciding with a real one. For the quadratures under discussion the number of derivatives eliminated determines the order of the contact of the two curves at the extremities of the arc to be integrated, and also a minimum number of common points on the two curves. By division of  $h$  the number of common points is increased in simple proportion to the number by which  $h$  may be divided, but the order of contact at the extremities is not affected by this process. The remainder, on the other hand, is inversely proportional to a power of the number by which  $h$  is divided, a power greater by one than the order of the retained derivative.

In order to test the accuracy of formulæ for mechanical quadrature it is clearly necessary to take a difficult example, for otherwise all reasonably good formulæ would show insignificant errors. For this purpose Bertrand selected

$$\int_0^1 \frac{\log(1+x)dx}{1+x} = \frac{\pi}{8} \log 2 = 0.27219\ 826.$$

The curve in this case rises sharply from the origin, passes through a maximum at  $x=0.7825\dots$  and then approaches the  $x$ -axis asymptotically. In general form it resembles the energy curve of the spectrum.

I have taken the same example using 8-place natural logarithms and an 8-figure computing machine, and get the following table of results in which I stands for the computed integral.

Formula.	$n$ .	$I = \frac{\pi}{8} \log 2 +$
1	2	+0.00181 206
2	4	-0.00002 363
3	6	-0.00000 545
4	8	-0.00000 154
5	10	-0.00000 060
6	12	$\pm$ 0.00000 000
7	12	+0.00000 001

The results for (6) and (7) are very satisfactory while those for the earlier formulæ could be greatly improved by taking  $n$  at a multiple of its minimum value. According to

Bertrand, Gauss's formula for  $n=4$  gives a result which is too small by 3 units in the seventh place, and thus tested it is intermediate in accuracy between (5) and (6)\*.

As an application of the formulæ here developed I may mention the double integral of the probability curve. By any of the more accurate formulæ (2) to (7) it may be shown that

$$\int_0^\infty dx \left[ 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx \right] = \frac{1}{\sqrt{\pi}}$$

or

$$\int_0^\infty dx \int_0^\infty e^{-x^2} dx = \frac{1}{2}.$$

In computing it 7-place values from Burgess's table were taken and the result obtained coincided with  $1/\sqrt{\pi}$  accurately to 7 places. This value is of interest in the analysis of diffusion.

Values of the probability integral itself are commonly arrived at by a somewhat intricate process, better fitted to yield a related set of values than a single one. By the formulæ given in this paper applied to tables of  $e^{-x}$  isolated values of the probability integral are readily determined †.

\* Rather curiously Weddle's rule applied to Bertrand's problem gives somewhat better results than (3). Furthermore, as this rule is deduced from Newton's interpolation formula it appears to err only by a small fraction of the sixth difference, when the seventh difference is negligible. As here deduced from Euler's equation the error should include fifth differences. While these facts are not incompatible the relations seem to need confirmation, and I have integrated  $e^x dx$  from  $x=-1$  to  $x=2.6$  taking  $h=0.6$ , and using values of  $e^x$  with 7 significant figures. By a separate computation I find the true value of the integral to be 13.09585 85938. Weddle's rule gives a value which is too great by 0.00064 while the value of the corrective term given in this paper for his rule is 0.00073 or about 9/8 of the real error. Formula (3) gives a value 0.00016 too great or 1/4 of the error of Weddle's rule and 2/3 as great as the value of the derivative term in (3).

† For  $x=0.7$ , Burgess's table (Trans. R. S. Ed. vol. xxxix. 1900, p. 257, gives a value of the probability integral greater by 2 in the seventh place than that assigned to it in Encke's table (*Ast. Jahrbuch*, Berlin, für 1834). This is founded on Kramp's table (*Analyse des réfractions astronomique et terrestres*, Leipsic et Paris, an VII. [1799]) and has been adopted by Airy, Kelvin, and others. A physicist not familiar with the history of these tables might wish to ascertain which value is correct, and this may be accomplished by the help of (5). With  $h=0.07$ , seven-place values of  $y=e^{-x^2}$  may be taken out of Smithsonian Math. Tables. Integrating by (5) and multiplying by  $2/\sqrt{\pi}$  gives the required integral at 0.6778012 which is Burgess's value. If a computing machine is available, the arithmetical work is no more extended than in the example worked out in a previous footnote, and it requires no mathematical knowledge beyond that required for interpolation to one additional place in the table of the exponential, so that a school-boy can do this "sum" on a single page of note-paper.



To many experimental physicists calculus is a thorn in the flesh and a weariness to the spirit, partly no doubt because they so constantly have to deal with functions whose exact mathematical expression is unknown or uncertain. I take leave to suggest that mechanical quadratures may serve them to reach conclusions which mathematicians would obtain more elegantly but in a less obvious way.

But it appears to me that there is also room for a methodical examination by mathematicians of the applicability of formulæ such as are developed in this paper to the integration of functions which cannot be integrated in "finite terms." In such an inquiry the main point would be to determine for each class of functions the limits of convergence of Euler's series and the nature of the substitutions most conducive to increase in convergence. I hope somebody may pursue the matter further.

Washington, D.C.  
April, 1911.

XXXIV. *On the Ratios which the Amounts of Substances in Radioactive Equilibrium bear to one another.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

ON page 40 of the last volume of this Magazine Mr. H. Mitchell has given a general solution of the system of differential equations representing the course of a series of consecutive radioactive transformations. This solution is then applied to the case in which the mean length of life of the primary parent substance is greater than that of any other member in the series. Mr. Mitchell's result is more general than the one usually cited, which depends on the assumption that the parent substance not only has the smallest rate of decay, but that this rate is negligible as compared with any other in the series.

It appears worth noting that the solution given by Mr. H. Mitchell is capable of still more general interpretation. For if the  $m$ th substance is the longest lived, we find, by a process precisely similar to that given in the communication referred to,

$$\frac{x_n}{x_m + x_{m+1} + x_{m+2} \dots + x_n} = \frac{\lambda_m}{\lambda_n}, \text{ when } n > m,$$

and  $x_n = 0$ , when  $n < m$ .

*Phil Mag.* S. 6. Vol. 22. No. 128. Aug. 1911. 2 A

Hence, after a steady state is reached, this case is experimentally undistinguishable from that considered by Mr. Mitchell. What appears to be the primary parent substance is certainly the most slowly decaying in the series, but whether it is preceded by others of more rapid disintegration we are not able to tell.

We may, if we choose, regard the relative frequency of the several types and species of organisms or other material components of an evolving system, when a steady distribution is reached, as a measure of their respective "fitness," or adaptation to the existing conditions. From this point of view any members of a radioactive series, for which  $n < m$ , appear as aggregates wholly unadapted to present conditions, or having a "fitness" zero. They would thus correspond to the "extinct" species of biology.

Yours faithfully,

New York,  
May 30, 1911.

ALFRED J. LOTKA.

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### XXXV. *Notices respecting New Books.*

*Bulletin of the Bureau of Standards.* Washington Government Printing Office, 1911. Vol. VII. Nos. 1 and 2.

SEVERAL important papers are contained in these two parts. Messrs. Waidner and Burgess discuss the Temperature scale between  $100^{\circ}$  and  $500^{\circ}$  C. The authors have determined the boiling-points of naphthaline and benzophenone on the temperature scale defined by the platinum resistance-thermometer calibrated in ice, steam, and sulphur vapour ( $444^{\circ}\cdot70$  on the const. vol. Nitrogen thermometer). These two vapours give B.P.'s of  $218^{\circ}\cdot0$  and  $306^{\circ}$  C. respectively on the Nitrogen scale to a probable accuracy of one-tenth degree. Messrs. Nutting & Tugman detail investigations on the Intensities of some H, Ar, and He lines in relation to current and pressure, the observations being made in Plücker tubes. Mr. J. H. Dallinger records an elaborate investigation on the temperature-coefficient of resistance of copper and the circumstances which tend to influence it.

In Part 2 Mr. W. W. Coblentz gives the results of experiments on the reflecting power of various metals, chiefly those used in electric lamps. The measurements were made in the cold, emphasis being laid on the recent work of Hagen and Rubens, in which it is shown that for wave-lengths less than  $4\mu$  the optical constants of metals vary slightly, if at all, with change in temperature, and this is the region of interest on the question of the

selective emission of incandescent lamps with metallic filaments. For tungsten the reflectivity is found to rise from 50 per cent. in the yellow to 89 per cent. at  $2\cdot5\mu$ , beyond which point it increases gradually to 96 per cent. at  $10\mu$ . Mr. W. W. Coblentz also makes a communication on the selective radiation from solids, in which in particular a study is made of the radiation from a Welsbach mantle. A remarkable difference is found between the behaviour of the mantle and that of the same material when operated as a solid glower heated electrically. The solid glower may emit  $8\cdot5$  times as much energy as the gas-mantle in order to attain the same emissivity in the green. The general conclusion is that it is highly probable that the radiation from the Welsbach mantle is purely thermal. No. 2 also contains an account of some experiments with coupled high-frequency circuits and some measurements of electrical oscillations in receiving antennæ by L. W. Austin.

*U.S. Department of Commerce and Labor. Coast and Geodetic Survey. Directions for Magnetic Measurements by DANIEL L. HAZARD.*

Washington: Government Printing Office, 1911. 8vo, pp. 131.

THIS may be regarded as embodying the official instructions issued to magnetic observers in the United States by the Government Department entrusted with the magnetic survey work. The volume describes the absolute magnetic instruments—magnetometers, dip circles and inductors—used by the Survey on land or sea, and explains the methods of determining constants and of taking and reducing observations. Instructions are given as to the selection of field stations and the most favourable conditions under which to observe. The Survey has several magnetic observatories under its control, and the volume thus naturally contains a description of the magnetographs employed and the methods of standardising and tabulating the curves. At the end there are 9 tables for use in reducing the observations and 3 giving a summary of regular diurnal variation results for the Survey's observatories at Sitka, Cheltenham, Honolulu, and Porto Rico.

## XXXVI. *Intelligence and Miscellaneous Articles.*

### ON THE LAWS OF MOLECULAR ATTRACTION.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a paper published in the *Phil. Mag.* of July Mr. Mills compares the results of his investigations on the laws of molecular attraction with some of those obtained by myself. The paper was written when Mr. Mills had not seen some subsequent papers I published on the subject, in which the relation between his

results and mine is pointed out and discussed. The results are not antagonistic if put into their proper place with respect to one another. As the subject is one of great importance and it is necessary that some fundamental ideas about it should once for all be settled, I beg to be permitted to emphasize a few of the points contained in the papers mentioned.

In investigations of the nature of the law of attraction between molecules giving rise to the internal heat of evaporation and surface tension, it is obvious that the investigation should be mathematically sound. Thus it is not only necessary that the formulæ deduced from the law assumed should agree with the facts, but it must also be shown that no other law can exist. Now I have shown that the law deduced must contain an arbitrary function (*Phil. Mag.* Jan. 1911, p. 83). This result is based on no assumptions whatever, but is a mathematical consequence of the nature of the heat of evaporation and surface tension. It follows therefore that we can obtain an infinite number of laws of attraction each of which gives rise to formulæ agreeing with the facts, which correspond to different forms of the arbitrary function, but we cannot be sure that any one of the laws is the true one without further evidence. Thus the inverse square law of Mr. Mills is obtained by giving the arbitrary function a certain form, which also determines the constant in his formula for the heat of evaporation, giving a good agreement with the facts. But it can be easily shown that the law cannot be true, for if it were the attraction is that of gravitation and it can be shown that this cannot account for the magnitude of the heat of evaporation (*loc. cit.* p. 89). In the paper Mr. Mills refers to the arbitrary function was put equal to a constant to see what agreement with some of the facts is obtained on this supposition, but it was not pointed out in that paper that it is arbitrary.

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Mr. A. Batschinski in a letter published in the *Phil. Mag.* of July points out that the formula  $\frac{L}{\rho_1^2 - \rho_2^2} = \text{constant}$ , where  $L$  denotes the internal heat of evaporation, appeared in a paper of his published previously to one of my papers in which it was given. I am sorry I missed seeing it. But I would like to point out that I did not obtain the formula empirically as he did, but by giving the arbitrary function in the law of attraction discussed above a certain form, which determines the nature of the above constant, and therein lies its principal interest (*Phil. Mag.* Oct. 1910, p. 678, and Jan. 1911, pp. 98-99).

Yours faithfully,

R. D. KLEEMAN.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

SEPTEMBER 1911.

XXXVII. *The Age of the Earth.* By J. JOLY, F.R.S.\*

[Plate III.]

THE recent contributions to the data bearing on the subject of the age of the earth have strengthened the evidence derived by two very different methods of computation; that based on the study of solvent denudation and that based on the accumulation of radioactive waste-products in minerals. While the indications of both lines of inquiry seem individually rendered more definite by these advances, the divergence in their final results have, if anything, become intensified. I propose in the following pages to review the opposing methods, as briefly as the many details permit, and to discuss the possibility of reconciliation.

I. *The Age of the Ocean derived from Solvent Denudation.*

Three recent contributions to this subject have appeared: That contained in Professor Sollas' Presidential Address to the Geological Society of London, 1909; in a paper on "A Preliminary Study of Chemical Denudation," by F. W. Clarke (Smithsonian Miscellaneous Collections, vol. lvi. June 1910); and in one by G. F. Becker on "The Age of the Earth" (Smithsonian Miscellaneous Collections, vol. lvi. June 1910).

\* Communicated by the Author.

*Phil. Mag.* S. 6. Vol. 22. No. 129. Sept. 1911.

2 B

These recent discussions chiefly centre round the ascertainment of the true present rate of supply of sodium to the ocean. The limitations of the method are also discussed.

My own original estimate of the age of the ocean\* was based on the only data then available—the estimates made by Sir John Murray of the average chemical composition of river-water and the probable total annual discharge of the rivers into the ocean. Calculating from its estimated volume and mean chemical composition, the mass of sodium now in the ocean, and dividing this by the calculated amount of sodium entering annually from the rivers, the uncorrected age of 99·4 million years was obtained. To this I applied certain corrections, to some of which I shall refer later. The final result of these corrections left the age as from 80 to 90 million years.

Professor Sollas approaches the question by a recalculation of the average amount of sodium discharged by the rivers annually. He finds that the added results available, as derived from the rivers of North and South America and Europe, give the uncorrected age as 78 million years. After a careful and detailed discussion of the corrections, Sollas concludes that the age lies between 80 and 150 million years; the latter figure being based on extreme assumptions.

Clarke bases his discussion of the question upon what he terms the *denudation factor*, i. e. the number of metric tons annually removed in solution from a square mile of drainage area. This is estimated for a number of important rivers of the world, accounting in this way for a drainage area of 28 millions of square miles out of the total of about 40 millions which drain to the ocean. The mean value found for the denudation factor is 68·4 tonnes. Assuming that this denudation factor is a fair average for the whole, the entire matter in solution discharged into the ocean in a year is 2735 millions of tonnes. From the chemical analyses of this saline matter for the several rivers, an average composition for each continent is found. When this is weighted for the quantity of water contributed by each continent, a final weighted mean composition is obtained which may be applied to determining the integral of the sodium passing annually from rivers to ocean. In this way it is found that 175,040,000 metric tons of sodium are annually discharged into the sea. Clarke next finds the total amount of sodium in the ocean to be  $14,130 \times 10^{12}$  tonnes. My own results were based on a slightly higher value— $15,611 \times 10^{12}$  tonnes. From his figures, Clarke now gets the uncorrected age as 80,726,000 years.

\* Trans. R. Dubl. Soc. vol. vii. 1899.

Although the numerous analyses which go to build up this result are not of equal value, there are certain satisfactory features in the computation.

It is explained by Clarke that in the wonderfully detailed analyses of the Mississippi by Dole and Stabler, taken along with their work on other great rivers of N. America, and with the observations of Forbes and Skinner for Colorado, data have been obtained for the United States which are not likely to be much altered by any future analyses. Twenty-two river-basins enter into the mean for the United States, giving a mean denudation factor of 79 tonnes. For the rest of N. America an estimate only is possible; but, for reasons given, Clarke concludes that "if we assume that six millions of square miles of N. America lose 79 metric tons in solution per square mile per annum, and that the composition of the saline matter so transported is that found for the United States alone, we shall not be very far from the truth." Possessing, thus, a standard based on the drainage of a great continent, we feel confidence in our criticism of other data. The quantity of water thus dealt with is rather more than one fourth of that supplied by the entire drainage areas of the earth.

It will be seen from the tables given by Clarke, that the mean denudation factor of 68.4 tonnes is in good agreement with the standard result from N. America, nor is it very largely departed from by the factors derived from other continents.

There can, I think, be little doubt that the results arrived at by Clarke and Sollas are not likely to be seriously disturbed in the future. It is most improbable that they require amendment to the extent of 50 per cent. This being so, we conclude that the uncorrected estimates of the age of the ocean as based on solvent denudation is of the order of 100 million years. It remains now to consider the legitimate corrections to be applied to this figure.

At the present moment the most important aspect of this method of evaluating the age of the ocean is involved in its degree of reliability as affording a *maximum* value of the time elapsed since solvent denudation began. This point I shall, therefore, specially consider.

The errors affecting the crude result found by dividing the sodium of the ocean by the annual river supply, and tending to make this estimate too small, are:—

- (a) Under-estimation of the sodium now in the ocean.
- (b) Neglect of sodium which at some period in the past may have been in the ocean, but is now removed from it.

(c) Over-estimation of the legitimate river supply of sodium.

(d) Decreased river supply of sodium in the past.

Of these possible sources of error (a) may be at once dismissed. The average depth and area of the ocean, and its average chemical composition, are sufficiently well known to preclude the possibility of any serious error.

In considering (b) it is necessary to bear in mind the magnitude of the quantities involved. The saline matter in the ocean would represent a volume of over 4,800,000 cubic miles, on Clarke's estimation. I have formerly pointed out that the rock-salt alone would suffice to cover the land area of the Globe to a depth of 122 metres. In comparison with quantities so vast all the salt deposits known sink into insignificance; nor is it likely that deposits adequate to enter into consideration exist.

The errors referred to in (c) must be of the nature of cyclic sodium: that is sodium which circulates from the sea to the land and back through the rivers to the ocean. Cyclic sodium exists in the form of wind-borne spray which descending on the land with the rainfall augments that which is truly derived by denudation. In arid regions it may settle as dust, to be, under special circumstances, washed ultimately into the sea. Again, the sodium which the rivers may derive from the ancient salt deposits which have been impounded from the sea is cyclic.

The influence of wind-borne sodium has been fully discussed by Sollas, Clarke, and Becker. There can be no doubt that it is relatively unimportant. My own original correction was 10 per cent. of the river supply. Becker by examining typical cross-sections of the isochlors, determined for the rainfall of Western North America by the U.S. Geological Survey, finds that an allowance of 6 per cent. is sufficient. Sollas shows that these isochlors indicate that but a small fraction of the sodium chloride of the American rivers can be referred to this source. Clarke, by a somewhat different line of attack, concludes that a correction of 7 per cent. on the sodium conveyed by the rivers of the United States is a maximum allowance. Clarke further considers that a correction for sodium chloride carried as dry dust is unnecessary.

In a paper contributed by me to the *Geological Magazine* (May 1900) I considered the possibility of oceanic sodium existing disseminated in the sedimentary rocks. Such sodium would be, of course, cyclic. It was easy to show that, even



on excessive estimates of the occluded sodium chloride in such rocks, taken in conjunction with their rate of removal by denudation, this source of supply to the rivers is less than 1 per cent. Clarke reconsiders the question and finds the allowance would not be more than 1 per cent. Three per cent. is regarded by Clarke as a maximum deduction for sodium artificially supplied in modern times to the rivers.

Oceanic salt deposits are not very abundant over the surface of the earth, being generally confined to particular formations. That they seriously affect the river analyses of all the great rivers of the world is in the highest degree improbable. In any case if we deduct all the chlorinated sodium from the river supply we must include also all sea-derived sodium. If we effect this calculation, we obtain an age of about 150 million years. I do not think it will be disputed that this figure is in its nature excessive.

There remains the possibility (*d*) that the assumed uniformity of past and present conditions is illusory: in other words, that special conditions now exist tending to bring about an abnormally great river supply of sodium.

The present is admittedly a period of large land exposure. This, however, involves a fact which must be held in mind. At the present time the land area actually draining into the ocean is about 39.7 millions of square miles. The total land area is, however, rather over 55 millions of square miles. It follows that about 30 per cent. of the land area contributes nothing to the ocean. The areas which are classed as "rainless," that is which have less than an annual rainfall of 10 inches and have no run-off, amount to one-fifth of the whole. Under such circumstances transgression of the ocean upon the land simply results in the diminution or disappearance of the great continental desert regions. It has been shown by Murray that it would require a vertical depression, relatively to the ocean, of 600 feet in order to reduce the existing land area by 26.7 per cent. Penck on the same data concludes that a submergence of 200 metres would reduce the area 29 per cent. A submergence of nearly 1500 feet is required to diminish the land area 50 per cent.

It is for geologists to judge whether world-wide transgressions of these magnitudes obtained for any long periods in the past. So far as I know, Palæography would not support such transgressions. A recent study of the Palæography of N. America by C. Schuchert (*Bull. Geol. Soc. Am.* vol. xx. 1910) leads to the conclusion that the mean area of that continent throughout the past has been about 8/10ths of

its present area. In his *Traité de Géologie*, De Lapparent, in a series of well-known restorations of ancient geography, shows how far, as judged by the sediments, there was transgression of the sea upon the land at various epochs. It does not appear that we can infer, even at the climax of the great Cenomanian transgression, that the existing land was at any time covered to one half its extent. And mindful of the fact that the area of denudation is in most cases much greater than that of deposition, when the latter is greatest the necessity of accounting for the former involves the assumption that tracts of land now submerged were then exposed. Without assuming the former existence of lost continents in the central oceanic basins, there seems very strong evidence for the disappearance of former land. The evidence is found in our own Islands, in N. America, in India, South Africa and Australia, and elsewhere. We have to recognize continual fluctuations, but the evidence for a prevailing reduction of continental areas by as much as 50 per cent., or even 25 per cent., in the past is, so far as I know, not forthcoming. We might go further and state that so great a diminution of existing land area as 50 per cent. certainly *did not* prevail in the past. Such a reduction involves about 25 per cent. of the present rate of solvent denudation, and increases the age accordingly.

Meteorological conditions, unless occasioned by a prevailing change in the amount of solar heat, cannot be supposed to have steadily affected in one direction the rate of denudation. It is worthy of note that the testimony derived from the solvent denudation of the continents shows that climatal conditions do not, within the limits, seriously affect the rate of solvent denudation. This finds explanation in the extremely complex nature of the factors concerned in rock-weathering and rock-solution. Now the mere abundance of life throughout the world in every age since the Cambrian, and very certainly in pre-Cambrian times also, is sufficient indication that climatal conditions cannot have been so extreme as to seriously inhibit denudation. It would be easy to cite evidence from sun-cracked sediments dating back to Torridonian times, from teeming oceanic life now confined to tepid seas, but at various periods of geological history inhabiting every part of the ocean, and finally from forest growth and insect life on the land, that there is no evidence for continued lessened solar heat in past ages.

But existing soil-conditions might be exceptional. There are to-day great sheets of glacial clays spread over the

northern lands of the earth: may they not affect the river discharge of sodium? The answer is to be found in the river analyses. It is sufficient to refer to the figures cited by Clarke in his 'Data of Geochemistry.' There is no indication of excessive supplies from northern rivers.

I am not aware of any sources of error other than those now considered. It would appear that solvent denudation estimated in the only manner open to us assigns an age to the ocean which at its probable maximum does not exceed 100 million years. Assuming that certain sources of error combined to lower this age, for instance that more complete knowledge will reveal a lesser sodium supply than has been determined on existing data; that the cyclic sodium should be taken as somewhat more than we have assumed; that former fluctuations of land area on the whole produced an effect on solvent denudation: assuming all this we might be somewhat out in our reckoning. We have, however, neglected all those sources of error tending to *increase* the age unduly. Chief among these are the following:—Primitive sodium existing in the ocean: marine solvent denudation effected directly on the coasts and sediments: sodium supplied with volcanic ejectamenta: sodium supplied by submarine rivers and springs. For a discussion of these sources of error I must refer to the several papers cited above. It is generally conceded that any precise evaluation of their effects is not possible; so that a considerable margin must be left when considering the minor limit of the age of the ocean by this method. They certainly produce *some* effect as a set off to the corrections already dealt with. It is against probability to add 50 per cent. to the value already estimated as a major limit. We can only double it by appealing purely and simply to the imagination for effects of which we possess no indication, and the existence of which is at variance with what we know.

The age as determined is based upon the summation of the sodium supplied by the rivers during geological time. This integral can, obviously, give us no information as to the relative durations of the geological epochs. The latter question can be approached in two ways. (1) By means of the stratigraphical column or measured maxima of detrital and chemical deposits, assuming that these were laid down at an approximately uniform rate; and (2) by the radioactive method. I shall first consider the former method

II. *The Age from the Sedimentary Column.*

As the result of the observations of geologists in many parts of the world the maximum thickness of the strata deposited in the various geological periods may be estimated as follows :—

Recent and Pleistocene .....	4,000	
Pliocene .....	13,000	
Miocene .....	14,000	
Oligocene .....	12,000	
Eocene .....	20,000	
		63,000
Upper Cretaceous .....	24,000	
Lower " .....	20,000	
Jurassic .....	8,000	
Trias .....	17,000	
		69,000
Permian .....	12,000	
Carboniferous .....	29,000	
Devonian .....	22,000	
		63,000
Silurian .....	15,000	
Ordovician .....	17,000	
Cambrian .....	26,000	
		58,000
Keweenawan .....	50,000	
Animikian .....	14,000	
Huronian .....	18,000	
		82,000
Archæan .....	?	
Total .....		335,000 feet.

This compilation is due to Professor Sollas (Presidential Address, Geol. Soc. London, 1909).

It is not probable that there will be in the future any very large amendment of these figures so far as they refer to post-Algonkian time. The Jurassic, as Sollas observes, seems deficient. The pre-Cambrian is the most obscure among the estimates. It claims our special attention, not only with reference to the thickness of accumulated sediments, but in so far as the observations may throw light on the denudative conditions of the time.

In no part of the world are pre-Cambrian rocks better developed and exposed than in and around the Archæan shield of Canada ; and fortunately no rocks have been more carefully studied within recent years. The appearance of the monograph of Van Hise and Leith (Bulletin 360. U. S. Geol. Survey, 1909) places the known facts at our disposal along with explanatory remarks of the most helpful character.

It will be remembered that most American geologists now subdivide pre-Cambrian rocks as follows :—

ALGONKIAN.	{	Keweenawan.
		Upper Huronian (Animikian).
		Middle „
		Lower „
ARCHÆAN.	{	Laurentian.
		Kewatin.

Prior to 1904 the Lower and Middle Huronian were together called Lower Huronian. Alternative names for the three divisions of the Huronian are Lower, Middle, and Upper Marquettian. The lines represent unconformities.

A study of the recorded facts shows that the higher estimates of Keweenawan rocks include preponderating amounts of igneous rocks, both effusive and volcanic. The time value of these materials is probably—nay certainly—small. Van Hise cites a case where the accumulation of 7000 to 8000 feet of Huronian volcanic materials is paralleled by the collection elsewhere of 700 to 800 feet of ordinary sediments (*loc. cit.* p. 146). The estimates which approximate to as much as 45,000 feet include some 30,000 feet of igneous or mixed igneous and sedimentary materials (*loc. cit.* p. 191). No sedimentary column thicker than 17,000 feet is cited.

The Huronian, or lower division of the Algonkian, is nowhere, save in an early estimate of Winchell's, found to embody more than 15,000 feet of sediments. Winchell's estimate (*loc. cit.* p. 206) is obscured by the nomenclature, and would seem to include Archæan rocks. If his Marquettian, which name he applies to rocks formerly known as Kewatin, includes Lower Huronian only, we have an estimate of 27,000 feet for this division. The estimate would be unique. The highest distinct estimate of Lower Huronian which I have found in the Bulletin is "a possible maximum thickness" of 16,000 feet, of which 5000 feet are true sediments (*loc. cit.* p. 164).

The Algonkian generally is variously estimated, but in no case is a thickness greater than 50,000 feet cited. In the Cordilleras the Belt series—30,000 feet—plus the Cherry Creek series may amount to more. It does not seem likely, however. The former series is characterized by Van Hise and Leith as unique among the pre-Cambrian series of North America for wide extent, thickness, and lack of

deformation. There is no apparent unconformity between the Cherry Creek series and the gneissic rocks beneath. In the Selkirk Range 40,000 feet of deposited rock are recorded, but the correlation is somewhat obscure, suggesting that its age may not be entirely pre-Cambrian. In Nova Scotia sedimentary rocks, probably Algonkian, amount to 26,000 feet. The Canadian Huronian (equivalent to Algonkian) has been estimated up to 50,000 feet. It is largely volcanic, and contains unstratified igneous masses.

It is remarkable that recent work has in many cases tended to reduce the estimates of earlier observers. Chamberlin and Salisbury ('Textbook of Geology,' p. 257) point out the liability to over-estimation which exists in these cases. These same observers state ('Textbook of Geology,' p. 192) "The maximum thickness of the system (Keweenawan) has been estimated as nearly 50,000 feet, but it is not impossible that this estimate is an exaggerated one. If it be correct, the Keweenawan is the thickest body of post-Archæan rock referred to any one period. This seemingly incredible thickness may merely mean inclined deposition and subsequent tilting and shearing and the estimate be altogether correct." And of the proterozoic systems collectively in the Lake Superior region they write :—"If none of the estimates are exaggerated, there is an aggregate of more than 30,000 feet of sedimentary rock in the proterozoic systems" (p. 198).

It would appear then that the Keweenawan at its maximum, so far as observed, is less than 50,000 feet, and its true sedimentary thickness evidently considerably less. The Huronian does not appear to have been reliably estimated as above 15,000 feet. Together the maximum estimates for the Algonkian are not above 60,000 to 65,000 feet, *inclusive of igneous materials*. In its great development in the Cordilleras it would appear that a maximum of 40,000 feet of true sediments would be safe, on the existing data.

With the Archæan we are not here concerned. Van Hise and Leith briefly summarize our knowledge of the earlier rocks in these words :—"The Algonkian is characterized by well-assorted fragmental and chemical sediments giving evidence of extensive decomposition of land areas and of the passage of normal cycles of erosion. Igneous rocks are abundantly present, but for the most part are subordinate in amount to the sediments. The Archæan is characterized mainly by igneous rocks with the sediments in very small quantity. The Archæan sediments, moreover, are frequently of 'wacke' type, and, so far as known, are not largely of the cleanly assorted kinds resulting from

complete decomposition as in the Algonkian." (Pp. 21-22.) Similar testimony is borne by Chamberlin and Salisbury ('Text-book of Geology,' ii. p. 199).

According to the definition of Algonkian and Archæan we must draw a line at the base of the former as representing that limit at which geological time, as an era of sedimentation and solvent denudation, began. "The Archæan was essentially a period of world-wide vulcanism, and in the relative proportions of rocks of igneous and sedimentary origin represents a departure from the uniformity of conditions of later geological times" (Van Hise and Leith, *loc. cit.* p. 30).

Turning to the pre-Cambrian geology of other parts of the world we find that the Torridonian and Lewisian of North-west Scotland in their mutual relations and petrographical characters resemble the Algonkian and Archæan divisions of North America. The aggregate thickness of the Torridonian has been estimated at not less than 10,000 feet. To this the Dalradian has, possibly, to be added.

The pre-Cambrian rocks of Finland have been divided by Sederholm as follows:—

Jotnian.
<hr/>
Jatulian, Upper.
Jatulian, Lower.
<hr/>
Kalevian, Upper.
Kalevian, Lower.
<hr/>
Bottnian.
<hr/>
Ladogian.
Katarchæan.

Sederholm makes the same statement regarding the Jotnian, Jatulian, Kalevian, and Bottnian, as has been made with reference to the Algonkian.

Sederholm says:—"At least as far back as during Bottnian time the climatic conditions were not sensibly different from those of later geological periods, as shown by the existence of rocks which, in spite of their metamorphic character, show themselves to be sediments with the same regular alternation of clayey and sandy material (annual stratification) as the glacial clays of that same region, explainable only by assuming a regular *change of seasons*" (Sederholm, J. J., *Bull. Comm. Géol. de Finlande*, No. 23, p. 95, 1907).

The parallel suggested by Sederholm with the Lake Superior rocks is as follows:—

Jotnian equivalent to Keweenawan.

Jatulian           ,,           Animikian or Upper Huronian.

Kalevian           ,,           Lower Huronian.

Van Hise and Leith further suggest the correlation of the Ladogian and Katarchæan with the Kewatin and Laurentian; the Ladogian being intruded by the granites and gneisses of the Katarchæan.

In China a basal complex of gneisses having very subordinate masses of sedimentary materials underlie four sedimentary groups, originally muds, grits, conglomerates, and limestones: having, in fact, all the characteristics of the Algonkian. In short this prevailing relation of an older gneissic and dominantly igneous system with an unconformably overlying metamorphosed sedimentary and volcanic series—which again is divided by unconformities—is a significant feature observed in many widely separated parts of the world.

The above cited facts seem to show (1) that we are entitled to commence our reckoning of the sedimentary column at the base of the Algonkian; (2) that the sedimentary deposits of that epoch are probably not greater than the more or less concordant observations from several localities indicate; (3) that the early sedimentation was similar in character to that which proceeded in subsequent periods.

Although much is gained if we may regard these deductions as secure, it is difficult to determine any approximate time-equivalent for these ancient deposits. It is true that there is no reason to suppose that their derivation proceeded at a different rate from more recent ones; their rate of accumulation, however, may have been, and, indeed, probably was, quickened by less stable crust conditions, permitting more localized depressions and greater concentration. The disposition of the earlier sediments sometimes affords evidence of this. There are, again, several unconformities in the pre-Cambrian succession which do not appear to be represented in the known sedimentary accumulations. Van Hise and Leith recognize the principal unconformity as separating the Archæan from the Algonkian. Adams, however, recognizes one of equal significance beneath the Upper Huronian. Three unconformities occur within the Algonkian. That these are indicative of considerable lapses of geological time is highly probable.



A discussion of the time-allowance for these early unconformities would lead us too far into speculation. It may be observed, however, as regards the evidence for prolonged periods of denudation deduced from regional base-levelling, that the instability of the early crust must again be kept in mind. It is probable that the Algonkian mountains were not of the dimensions of those of later periods and that, therefore, they were at once more rapidly formed and more rapidly removed. Van Hise and Leith suggest that the unconformities may represent as much sediment again as now remains to observation. This, of course, can only be matter of opinion; and I have as far as possible endeavoured to exclude what is purely matter of opinion from this review of the subject. It would seem, however, that Sollas' estimate of 82,000 feet of sediment includes such an allowance as appears possible to Van Hise and Leith.

Taking all into account—and much has been omitted which might be said upon the subject—it does not appear that Professor Sollas' compilation of the stratigraphical column need be seriously disturbed. If we double the estimate for the Jurassic we at least tend to reduce the possibility of error of deficiency in the thickness assigned to this system. This brings the column up to, say, 345,000 feet.

What now, finally, is the time value of this enormous total? Unfortunately the average rate of collection is a very indeterminate quantity. We are, I believe, at liberty to assume that the rate of deposition and sinking was anything from, say, one foot to but a few inches in a century. A rate of accumulation of four inches in a century interprets the geological column as indicating 103 millions of years. Three inches gives us 148 millions. The order of the time-value is probably indicated in these figures.

It is important to note that the facts of solvent denudation place a quite definite limit on the amount of sediments which have been formed during geological time. The sodium which has reached the ocean has originated in the conversion of igneous into sedimentary rocks. It is easy to calculate from the composition of a generalized igneous and a generalized sedimentary rock and from the quantity of sodium in the ocean that the denudation of about 84 million cubic miles of igneous rock, producing about 60 million cubic miles of sediment, accounts for the sodium in the ocean. Such a quantity of sedimentary rock would, if all was now on the land, cover the present land area (55 million square miles) to a depth of a little over one mile. As it can be shown that somewhat less than a third of the sediments have been preci-

pitated as oceanic deposits, the average depth of the sedimentary rocks on the land is less than one mile; about 4000 feet. The total sedimentation throughout geological time must be restricted within this limit. Possibly the limit is too high, for there may have been some sodium in the primitive ocean. It is difficult to show wherein it is too low. This limit must define not only sediments which keep their recognizable characters as such, but those which may possibly have been metamorphosed beyond certain recognition. It is significant that the guesses (for they can only claim to be such) of several writers as to the amount of recognizable sediment upon the land areas, do not diverge very far from the suggested limits. Thus Van Hise thinks these rocks may be taken as on an average covering the continents to a depth of 2 kilometres. Clarke thinks that the sediments certainly do not occupy a bulk equal to the whole land extending above sea-level. This would amount to less than an average of 2411 feet deep over the continents. The sediments in the sea would be additional to this. ('Data of Geochemistry,' p. 29.) These estimates may be guesses, but it is improbable that they are several times in error. The observed amounts of sediment are not then in discord with the limitations imposed by solvent denudation.

### III. *The Age of the Earth by Radioactivity.*

The radioactive investigation of the age of the earth is based upon the accumulation in minerals of the inert products, helium and lead.

The rate of production of helium by a given amount of uranium may be regarded as known with considerable accuracy. It may be assumed that one gram of uranium in equilibrium gives rise to, closely,  $10.7 \times 10^{-8}$  c.c. of helium (measured under standard conditions) per year. Thorium and its products of change are just as wide-spread in occurrence as uranium. The contribution of helium derived from the thorium group must, therefore, in most cases be also taken into account. Failing direct measurements of the rate of generation of helium by thorium, it is possible to estimate this in terms of the out-put due to uranium by a comparison of the ionization effects of the two families of substances. This comparison has been made by Boltwood. Allowance has further to be made for the different ionizing activity of the alpha rays from the uranium and thorium series due to their differing velocity and range. The final result is that 1 gram of thoria ( $\text{ThO}_2$ ) is equivalent, in its rate of production of

helium, to 0.203 gram of  $U_3O_8$ . The "helium ratio" of a mineral is the helium in cub. cms. per gram of "total equivalent" uranium oxide present. This is the usage adopted by Strutt. In a recent paper (Proc. R. S. Oct. 1910) Strutt experimentally verifies this procedure by direct measurement of the helium evolved by minerals rich in uranium and thorium.

The use of lead as a measure of geological time involves the assumption that Boltwood's theory is correct, *i. e.* that lead is the final product of decay in the uranium series. There is strong evidence in favour of this view. Notably the fact that the atomic weight of uranium, less that of the eight alpha particles which are known to be emitted during its several stages of disintegration, descends to that of lead. The universal association of the two elements and the connexion of this association with geological time, constitute further evidence.

The mass of lead generated in one year per gram of uranium is easily found from a knowledge of the mass of helium produced. The latter, calculated from the volume, is found to be  $1.88 \times 10^{-11}$  gram. The associated lead will be  $1.22 \times 10^{-10}$  gram. That is, the presence of one gram of uranium involves the production of  $1.22 \times 10^{-10}$  gram of lead per annum. A small correction may be required for the exhaustion of the uranium.

The most obvious criticism which the radioactive method suggests may be embodied in the following possibilities:—

(a) Risk of the original presence of helium or lead in the minerals investigated.

(b) Risk of loss of helium or lead, or their gain from spurious sources.

As regards the first of these heads there is evidence that helium or lead may be originally present in the substance. In fact, we may in a general way consider that the same causes which lead to the segregation of uranium or thorium most probably led to the concentration of other substances. This at least is probable where, as in the case of zircon, none of the substances dealt with are essential parts of the molecule of the mineral. The magma or menstruum from which the parent radioactive substances are derived may be very rich in helium or lead, and the amounts of these constituents which enter into the mineral may be considerable. It follows that the absolute value of the helium or lead ratio involves the events attending the genesis of the mineral. It is even quite probable that substances crystallized out within a plutonic mass, and which, at first sight, might be thought

secure from impurities of this sort, would be seriously affected. Consider the case of a mineral of early consolidation such as biotite. It is held by many petrologists that the substances first to crystallize are not necessarily those whose molecules were first formed in the magma. Biotite or hornblende may, indeed, crystallize in advance of felspar or quartz, but they do so in presence of already formed molecules of these bodies or of molecules which are forerunners of these bodies. If this were not the case the adjustment of the alumina to the potash, soda, and lime which appear in the felspars would be inexplicable\*. On this view a clear explanation is found of the heterogeneous concentration of elements in bodies of early consolidation. These minerals, in a sense, are residual, receiving those elements which have been excluded from taking part in earlier molecular grouping. The final result is a "forced isomorphism."

The same phenomena, on an intensified and more demonstrable scale, appear in the formation of pegmatitic minerals. Here very often it may be inferred that mother liquors rich in the rarer elements and the products rejected by the magma, generate on a large scale minerals which are quite subordinate within the mass of the rock. Extruded gases, under great pressure, also act under such conditions. In the internal cavities and druses of granites, doubtless, all these factors operate. Under such circumstances are generated the beryls and zircons which find their way into museum collections.

In keeping with the conditions attending vein minerals Strutt found that such minerals from the Cornish granite contained more helium, relatively to the radioactive elements present, than did the granite itself, although the vein must be younger than the rock containing it. The fact, also shown by Strutt, that beryls often contain a quite unaccountable quantity of helium, probably finds its explanation in the original occlusion of this substance.

Brögger, in writing of the syenitic pegmatites of Norway, concludes that the minerals of the thorite-orangite group, including urano-thorite, crystallized in the first phase of vein-formation, "that of magmatic consolidation with the cooperation of pneumatolytic processes," and that in the second and principal phase of pneumatolytic activity galena crystallized out. (Brögger, *Die Mineralien der Syenitpegmatitgänge*, pt. 1, pp. 160, 164, and pt. 2, p. 10.) If the

\* Harker, 'The Natural History of Igneous Rocks,' London, 1909, p. 167.

undifferentiated magma has been fairly radioactive, may not the pegmatitic substances, representing a large part of the rejected elements of the magma, be rich in the products of radioactive decay? It would seem that we are reasonably entitled to expect this. There might even be a certain proportionality between the amounts of radioactive bodies and segregated products of decay.

The results of the experiments themselves alone can indicate how far sources of error of this kind have operated. The final ratio—whether of helium or lead—to the parent radioactive substance is, we may suppose, compounded of two ratios, a segregation ratio which obtained from the first, and a generative ratio which kept on increasing throughout geological time. Consider the case of lead. We have no *prima facie* right to conclude that the originally segregated lead is, relatively to the uranium, more for, say, Archæan minerals than for Devonian. If then the gross lead ratio for the former is very much greater than for the latter, the effect of the occluded lead must only exercise an insignificant influence in invalidating the results regarding Archæan time. To take a concrete example. The assumption that of the total lead found in Devonian minerals a quantity equal to two per cent. of the uranium present in each case is not of radioactive origin but was originally introduced, amounts to saying that one half the ratio (about) is due to original segregation and one half to radioactive genesis. The time value of the corresponding deduction from Devonian time (as derived from the gross ratio) is about 160 million years. A quantitatively equal correction applied to the ratio observed in Archæan minerals will not be very important, as will presently be seen. Unless, then, we have some reason to infer that the conditions attending the formation of the minerals having the higher ratios were such as to lead to the inclusion of greater relative amounts of lead, the objection under this head is not of serious weight, at least in the case of the higher ages which have been arrived at.

Acting either to increase or diminish the observed deduced age, errors under the head (b) may exist. The volatile escape of helium has been demonstrated by Strutt. Under past conditions of heating and percolation, &c., its escape is very probable. Acting the other way, radium is known to migrate from its parent elements, and in considerable amounts. Lead is certainly at least equally liable to migration under suitable conditions. These sources of error would also tend to go on augmenting with the lapse of time. Unless, however, it can

be shown that a special sort of selective absorption for one or more of the elements likely to bring in error is exercised within the minerals dealt with, the error can be appraised at its true worth by comparative observations upon associated substances which do not contain appreciable amounts of the parent radioactive bodies, and which have been exposed to like vicissitudes of history.

The earliest determination of age by the radioactive method is, so far as I am aware, that made by Rutherford (*Phil. Mag.* Oct. 1906, p. 368). The helium in a specimen of fergusonite was determined by Ramsay and Travers as amounting to 1.81 c.c. per gram. The mineral contained about 7 per cent. of uranium. From this Rutherford deduced the age as about 240 millions of years. The geological position of this mineral is not specified, nor is the possible influence of thorium taken into consideration.

The principal development of the method by helium ratio is due to Strutt, whose work upon the subject has appeared in five papers in the *Proceedings of the Royal Society* (1908-1910). These experiments deal with phosphatized fossil remains and nodules, hæmatite and other iron ores, zircons, and sphenes. Some of these determinations are evidently not available as an estimate of the time since their formation, being plainly deficient in helium. Such results of course strengthen the conviction that loss of helium must occur in some cases.

The results arrived at by Strutt are not always concordant. Thus we find two sphenes of Archæan age and from the one locality (Renfrew Co.) affording 222 and 715 millions of years; and again two Archæan sphenes from the one locality (Twederstrand, Norway) 213 and 449 millions of years. Zircons show for Palæozoic time 140.8 to 321 millions of years. Here the lower figures are supported by results on hæmatite. This one mineral gives for the time since the Eocene age 30.8, since the Carboniferous 141, and since the Devonian 145 millions of years. Limonite gives for post-Carboniferous time 145 million years. These are closely agreeing results. Other iron ores give, however, inconsistent results. All are, of course, reconcilable if we assume that the lower results are in every case due to loss of helium. It is a little unfortunate in this connexion that the minerals used for the greater ages are more retentive in their nature (sphene and zircon) than the substances dealt with for determination of the lesser periods of time.

Strutt, in his final paper, selects from his results the

following as summarizing the data of his earlier papers :—

Sphærosiderite from Rhine Provinces. Oligocene ..	8.4 × 10 <sup>6</sup> years.		
Hæmatite, Co. Antrim. Eocene .....	31	"	"
" Forest of Dean. Carbonif. Limestone. .	150	"	"
Sphene, Renfrew Co., Ontario. Archæan .....	710	"	"

These are advanced as minimum values, the loss of helium being impossible to estimate.

Boltwood first investigated the age by the accumulation of lead (*Am. Journ. Sc.* vol. xxiii. 1907). Very high figures were obtained; ranging from 246 to 1320 millions of years. Becker criticizes these results (*Bull. Geol. Soc. Am.* vol. xix. p. 113, 1908), pointing out that certain radioactive minerals of well-determined age (Llano Group, not far below the Cambrian) afford on the same principles ages which are quite incredible, ranging from 1671 to 11,470 millions of years. Boltwood questions the suitability of the minerals on the score of incipient or advanced alteration. Becker in reply urges that there is no evidence to show that alteration can affect the ratios. Becker considers, further, that Brögger's views, as cited above, show that lead may be occluded as an impurity in such minerals, and that the amount of this impurity will vary from crystal to crystal, in accord with the results of the observations.

The subject of the lead ratio has been lately taken up by A. Holmes (*Proc. R. S.* June 1911). Holmes selects minerals from the intrusive nephelene syenite of the Christiania district, supposed by Brögger to be of middle or lower Devonian age; most probably the latter. Seventeen minerals are investigated, among which are thorite, biotite, zircon, ægerine, nepheline, felspar, &c. The ratio of lead to uranium ranges from 0.041 to 0.500. There is found to be an increase in the value of the ratio with diminution in the amount of uranium; a result suggesting the presence of original lead. Holmes, accordingly, rejects about half the results (those which give the higher ratios) and finds a mean among eight results which range from 0.043 to 0.050. The mean of these gives for post-Lower Devonian time 370 million years. It must be admitted that this result is not entirely satisfactory; it contains an element of arbitrary choice, and although it is possibly true that the minerals with least uranium contain too much original lead to be reliable, we are by no means sure that even larger amounts of original lead did not enter into the constitution of the others. The agreement among the ratios renders this improbable, however.

Holmes enters into the question of the geological positions of the results cited by Boltwood, and concludes that they may be tabulated as follows. His own mean result is included in the table.

Geological Period.	Pb/U.	Millions of Years.
Carboniferous .....	0.041	340
Devonian .....	0.045	370
Pre-Carboniferous .....	0.050	410
Silurian or Ordovician .....	0.053	430
Pre-Cambrian :—		
Sweden ..... {	0.125	1025
	0.155	1270
United States {	0.160	1310
	0.175	1435
Ceylon.....	0.20	1640

The Swedish minerals are from pegmatites of an age younger than Jatalian. The results obtained from them show, among 17 specimens examined, two well-marked groups, having the ratios tabulated. There is nothing in the rocks to indicate any difference in age. Of the United States minerals those having the lesser ratio are from granites intruded into the Llano group (Texas) of metamorphosed sediments. Their age is, therefore, younger than the sediments, which are early Algonkian. Those with the higher ratio are from Burnet Co. (Texas) and Douglas Co. (Colorado). The geological evidence is similar to that of Llano Co.

The evidence for the pre-Cambrian age of the Ceylon thorianite is the resemblance of the rocks to the fundamental complex of India. The tabulated values are the means of several results cited by Boltwood, some of which are in closer mutual agreement than others.

These results greatly transcend Strutt's in the antiquity they assign to Palæozoic and pre-Cambrian time. This fact can be explained by the escape of helium. The possibility of occluded lead entering seriously into such determinations will, doubtless, form the subject of future research. Meanwhile it seems improbable that the higher average ratios of the oldest minerals can find explanation in this manner. I have already dwelt sufficiently, in view of our very deficient knowledge, on these points.

The discordance between the radioactive indications of time and those derived from the stratigraphical column appears clearly when we plot one against the other (Plate III.). The



assumption made in plotting the sedimentary thicknesses is that these, *inter se*, are roughly comparable as regards the times of accumulation. As I have already pointed out, this seems probable save in the case of the earlier pre-Cambrian sediments, which we might expect would have been accumulated more locally. The thicknesses of the several strata I have laid out according to the data collected by Sollas. The radioactive times are plotted above the points on the base-line to which their geological positions assign them. We have from the lead ratios two early-Algonkian results and two post-Jatulian results. The Archæan results by helium and lead cannot be located on the base-line save by the indications of the other results.

If there was accord between the stratigraphical column and the radioactive data, the latter should be ranged on straight lines which necessarily pass through the origin (present time). We find them, however, ranged upon curves. I have plotted the age of the ocean as determined by solvent denudation; erecting for this purpose an ordinate of 150 millions of years at the beginning of Algonkian time. The curves for helium and lead flow into this line in recent periods.

If now we assume that the time indications of the lead ratios are correct, we are presented with the following alternatives as regards the amendment of the sedimentary column.

We assume that the stratigraphical column for post-Carboniferous time is in actuality much as we have plotted it, and draw a right line from the origin through the three results for the age of Carboniferous, Devonian, and Silurian-Ordovician periods, as derived from the lead ratio. This is equivalent to assuming that the error in the stratigraphical record is to be sought mainly in the pre-Cambrian records. We therefore plot the early Algonkian and post-Jatulian results on this line. We have now to make the following amendment on the recorded thicknesses of the pre-Cambrian sediments. Algonkian sediments rise from 82,000 feet to 381,000 and 441,000 feet, according to which of the two early-Algonkian results we select. Keweenawan sediments rise from 50,000 feet to 245,000 or 359,000 feet according as we select among the two Jatulian results.

While it is true that important unconformities exist in the pre-Cambrian succession, the sedimentation equivalents of which are not found as yet, it seems incredible that amounts of sediments nearly double the entire thickness of post-Algonkian rocks and from 70 to 80 miles in cumulative depth, can have escaped investigation. There is another

point. The calculation which equates the amount of sodium in the ocean with the estimated bulk of the detrital sediments, knowing the loss by solution attending the derivation of these from the average igneous rock, has, as we have seen, been found to give results in fair agreement with the measurements of all the quantities involved. The radioactive results must now postulate an amount of pre-Cambrian denudation far greater than the whole amount of sediment previously estimated would have given rise to. This point is really quite apart from the question of the age of the ocean. It is purely one of gain and loss, of balance of accounts. Nor can evasion of the difficulty be found by ascribing exceptionally local restrictions to pre-Cambrian denudation. It is probable that none was more world-wide in its effects.

If these conclusions appear untenable we may deal with the results in another way. The ages found from the higher lead ratios may be placed at a reasonable distance from the base of the Cambrian and joined by a right line to the origin. To bring them on to the line so determined the results for the Carboniferous, Devonian, and Silurian-Ordovician must be shifted to the left. This procedure is equivalent to assuming that while the total thickness ascribed to the stratigraphical column is approximately correct, the proportionate thicknesses assigned to pre-Carboniferous and post-Carboniferous strata are erroneous: too much has been assigned to the latter. The readjustment of the strata involves diminishing the post-Carboniferous deposits about 50 per cent., and increasing the pre-Carboniferous by nearly 40 per cent.

The assumptions involved in making these adjustments are inherently improbable, and it might be thought easier to assume that the time-values of the post-Carboniferous strata were, as compared with the earlier strata, less. This emendation requires us to assume that the more recent materials were laid down about three times as fast as the earlier.

These are the alternative modes of adjustment of radioactive time to the stratigraphical column, leaving the latter on the whole intact. If we assume that the recent sediments have been over-estimated in thickness, we can, by discarding about one half the recorded thicknesses since Carboniferous time, produce an effect on the diagram equivalent to moving the origin to the right. With this particular numerical assumption the lead line will become steeper than it appears on the chart, and the early-Algonkian point will remain at such a distance to the right of the Cambrian as will ascribe to the pre-Cambrian sediments a thickness equal to that of the whole post-Algonkian accumulation.

The important question is, of course, as to how far such assumptions are permissible consistent with any degree of probability. There is much that is uncertain about data respecting rock thickness, not only as regards the actual field observations, but as to the real significance of what is observed. Again, the relative time equivalents of deposited rocks are not really known to us. Whether it is a detrital sediment forming in an estuary or a coral-reef building in clear water, the rate of growth must depend to some extent on the downward movement of the sea-bottom; either induced by the load or taking place from other causes. Some sediments, are, however, plainly of rapid and some of slow growth. Amidst such considerations we find no very definite grounds for numerical computation. So far as crustal yielding affects the question, the probable inference is, as I have stated above, that the earlier strata were in their greatest development more localized, and hence their time value should be less than the more recent. As regards the vertical distribution of definitely fast or slow collecting materials, a careful comparison of the materials throughout the geological column is required in order to gather any evidence that may be forthcoming from these indications. At present, however, there seems nothing to support the different time values or amended thicknesses which must be assumed if we are to adjust the radioactive results in any way to the sedimentary record.

What will *prima facie* appear most difficult to credit in the foregoing assumptions is the extremely slow rate which must be ascribed to the accumulation of the sediments even at their maximum. If the recorded depths of sediment have taken 1400 million years to collect, the average rate has been no more than one foot in 4000 years! This seems incredible: and if we double the depth of maximum sedimentation it still remains incredible. But, if possible, still more incredible is the conclusion respecting solvent denudation to which radioactive time drives us. If the sodium in the ocean has taken 1400 million years to accumulate, the rivers are now bearing to the sea about 14 times the average percentage of the past—not less than 9 times. It seems quite impossible to find any explanation of such an increase.

With these difficulties in view it is excusable to direct attention to the foundations of the radioactive method and ask how far they are secure. The fundamental assumption is that the parent radioactive substance, uranium, has always in the past disintegrated at the present rate. Is this assured? I am not now suggesting that the rate of change has been affected by heat or pressure, but I assume that there may

have been a different and, from the evidence as well as from probability, a *greater* rate of decay in the past, arising intrinsically, and ultimately due possibly to conditions of origin.

I venture to suggest—I do so with diffidence—that our assumption of a constant rate of change for the parent substances—uranium or thorium—is really without any very strong basis. It rests upon analogy with the behaviour of the substances which have been derived from them. But there may be a very profound distinction. The latter are of radioactive origin. That particular distribution of stability or of intrinsic energy among the atoms of these bodies obtaining at the moment of their formation, upon which the subsequent constant change-rate depends\*, may be conditioned by the events of radioactive transformation, or by their past history, or by both. In a word, a radioactive origin may be essential.

Now we know nothing as to the origin of the primary radioactive elements. No substances of greater atomic weight are known from which they may be derived. Nor is it unphilosophic to assume that they have had some other mode of origin, seeing that the radioactive ascent must terminate somewhere. Uranium cannot be regarded, therefore, as in all senses one of a series any more than we should regard lead as such.

The matter seems to turn upon the legitimacy of the assumption that the mere existence of radioactive change progressing in a substance involves such a particular distribution of instability among its atoms as will ensure that a constant fraction of these disintegrate each unit of time, from their first origination—however this was brought about—till all are transformed. If such an hypothesis is not sufficiently secure to overbear the opposing evidence, we must agree to judge the former by the latter. In this case the accumulation of transformation products in minerals, in place of being a measure of geological time, serves to shed light upon the rate of transformation of the primary radioactive bodies in the past. Apart from its interest in other respects, the importance of such a conclusion to geological science would be great. If we supposed the curve, found by plotting the time results derived from lead-ratios against the sedimentary thicknesses, represented an approximation to the facts, the rate of change of uranium 150 million years ago may have been many times what it now is. The radiothermal effects of the whole series must have been proportionately increased, and the convergence of the radioactive activity must have had an influence upon the secular cooling of the earth.

July 18, 1911.

\* See Sir J. J. Thomson's Presidential Address to the British Association, 1909.

XXXVIII. *Problems in the Conduction of Heat.*

By Lord RAYLEIGH, O.M., F.R.S.\*

THE general equation for the conduction of heat in a uniform medium may be written

$$\frac{dv}{dt} = \frac{d^2v}{dx^2} + \frac{d^2v}{dy^2} + \frac{d^2v}{dz^2} = \nabla^2 v, \quad . \quad . \quad . \quad (1)$$

$v$  representing temperature. The coefficient ( $\nu$ ) denoting diffusibility is omitted for brevity on the right hand of (1). It can always be restored by consideration of "dimensions."

Kelvin† has shown how to build up a variety of special solutions, applicable to an infinite medium, on the basis of Fourier's solution for a point source. A few examples are quoted almost in Kelvin's words:—

I. Instantaneous simple point-source; a quantity  $Q$  of heat suddenly generated at the point  $(0, 0, 0)$  at time  $t=0$ , and left to diffuse through an infinite homogeneous solid.

$$v = \frac{Q e^{-r^2/4t}}{8\pi^{3/2} t^{3/2}}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $r^2 = x^2 + y^2 + z^2$ . [The thermal capacity is supposed to be unity.] Verify that

$$\int_{-\infty}^{+\infty} \int \int v \, dx \, dy \, dz = 4\pi \int_0^\infty v r^2 \, dr = Q;$$

and that  $v=0$  when  $t=0$ ; unless also  $x=0, y=0, z=0$ . Every other solution is obtainable from this by summation.

II. Constant simple point-source, rate  $q$ :

$$v \left[ = q \int_0^\infty dt \frac{e^{-r^2/4t}}{8\pi^{3/2} t^{3/2}} \right] = \frac{q}{4\pi r} \quad . \quad . \quad . \quad . \quad (3)$$

The formula within the brackets shows how this obvious solution is derivable from (2).

III. Continued point-source; rate per unit of time at time  $t$ , an arbitrary function,  $f(t)$ :—

$$v = \int_0^\infty d\chi f(t-\chi) \frac{e^{-r^2/4\chi}}{8\pi^{3/2} \chi^{3/2}} \quad . \quad . \quad . \quad . \quad (4)$$

\* Communicated by the Author.

† Compendium of Fourier Mathematics, &c., *Enc. Brit.* 1880; Collected Papers, vol. ii. p. 44.

IV. Time-periodic simple point-source, rate per unit of time at time  $t$ ,  $q \sin 2nt$  :—

$$v = \frac{q}{4\pi r} e^{-\sqrt{n} \cdot r} \sin [2nt - n^{\frac{1}{2}} \cdot r]. \quad . \quad . \quad . \quad (5)$$

Verify that  $v$  satisfies (1) ; also that  $-4\pi r^2 dn/dr = q \sin 2nt$  where  $r=0$ .

V. Instantaneous spherical surface-source ; a quantity  $Q$  suddenly generated over a spherical surface of radius  $a$ , and left to diffuse outwards and inwards :—

$$v = Q \frac{e^{-(r-a)^2/4t} - e^{-(r+a)^2/4t}}{8\pi^{3/2} a r t^{1/2}}. \quad . \quad . \quad . \quad (6)$$

To prove this most easily, verify that it satisfies (1); and further verify that

$$4\pi \int_0^\infty v r^2 dr = Q;$$

and that  $v=0$  when  $t=0$ , unless also  $r=a$ . Remark that (6) becomes identical with (2) when  $a=0$ ; remark further that (6) is obtainable from (2) by integration over the spherical surface.

VI. Constant spherical surface-source; rate per unit of time for the whole surface,  $q$  :

$$v \left[ = q \int_0^\infty dt \frac{e^{-(r-a)^2/4t} - e^{-(r+a)^2/4t}}{8\pi^{3/2} a r t^{1/2}} \right] \\ = q/4\pi r \quad (r > a) \quad = q/4\pi a \quad (r < a).$$

The formula within the brackets shows how this obvious solution is derivable from (6).

VII. Fourier's "Linear Motion of Heat"; instantaneous plane-source ; quantity per unit surface,  $\sigma$  :—

$$v = \frac{\sigma e^{-x^2/4t}}{2\pi^{1/2} t^{1/2}}. \quad . \quad . \quad . \quad . \quad (7)$$

Verify that this satisfies (1) for the case of  $v$  independent of  $y$  and  $z$ , and that

$$\int_{-\infty}^{+\infty} v dx = \sigma.$$

Remark that (7) is obtainable from (6) by putting  $Q/4\pi a^2 = \sigma$ , and  $a = \infty$ ; or directly from (2) by integration over the plane.

In Kelvin's summary linear sources are passed over. If an instantaneous source be uniformly distributed along the axis of  $z$ , so that the rate per unit length is  $q$ , we obtain at once by integration from (2)

$$v = \int_{-\infty}^{+\infty} \frac{q \, dz \, e^{-(z^2+x^2+y^2)/4t}}{8\pi^{3/2} t^{3/2}} = \frac{q \, e^{-(x^2+y^2)/4t}}{4\pi t} \quad (8)$$

From this we may deduce the effect of an instantaneous source uniformly distributed over a circular *cylinder* whose axis is parallel to  $z$ , the superficial density being  $\sigma$ . Considering the cross-section through Q—the point where  $v$  is to be estimated, let O be the centre and  $a$  the radius of the circle. Then if P be a point on the circle,  $OP=a$ ,  $OQ=r$ ,  $PQ=\rho$ ,  $\angle POQ=\theta$ ; and

$$\rho^2 = a^2 + r^2 - 2ar \cos \theta,$$

so that

$$v = \int_0^{2\pi} \frac{\sigma a d\theta \, e^{-\rho^2/4t}}{4\pi t} = \frac{\sigma a}{2t} e^{-\frac{r^2+a^2}{4t}} I_0\left(\frac{ra}{2t}\right), \quad (9)$$

$I_0(x)$ , equal to  $J_0(ix)$ , being the function usually so denoted. From (9) we fall back on (8) if we put  $a=0$ ,  $2\pi a\sigma=q$ . It holds good whether  $r$  be greater or less than  $a$ .

When  $x$  is very great and positive,

$$I_n(x) = \frac{e^x}{\sqrt{(2\pi x)}}, \quad \dots \quad (10)$$

so that for very small values of  $t$  (9) assumes the form

$$v = \frac{\sigma a}{2\sqrt{(\pi rat)}} e^{-\frac{(r-a)^2}{4t}},$$

vanishing when  $t=0$ , unless  $r=a$ .

Again, suppose that the instantaneous source is uniformly distributed over the *circle*  $\xi=0$ ,  $\xi=a \cos \phi$ ,  $\eta=a \sin \phi$ , the rate per unit of arc being  $q$ , and that  $v$  is required at the point  $x, 0, z$ . There is evidently no loss of generality in supposing  $y=0$ . We obtain at once from (2)

$$v = \int_0^{2\pi} \frac{q \, a \, d\phi \, e^{-r^2/4t}}{8\pi^{3/2} t^{3/2}}, \quad \dots \quad (11)$$

where

$$r^2 = (\xi - x)^2 + \eta^2 + z^2 = a^2 + x^2 + z^2 - 2ax \cos \phi.$$

Thus

$$v = \frac{qa}{4\pi^{1/2} t^{3/2}} e^{-\frac{a^2+x^2+z^2}{4t}} I_0\left(\frac{ax}{2t}\right), \quad \dots \quad (12)$$

from which if we write  $q=\sigma \, dz$ , and integrate with respect to  $z$  from  $-\infty$  to  $+\infty$ , we may recover (9).

If in (12) we put  $q = \sigma da$  and integrate with respect to  $a$  from 0 to  $\infty$ , we obtain a solution which must coincide with (7) when in the latter we substitute  $z$  for  $x$ . Thus

$$\int_0^\infty a da e^{-a^2/4t} I_0\left(\frac{av}{2t}\right) = 2t e^{x^2/4t}, \quad . \quad . \quad (13)$$

a particular case of one of Weber's integrals\*.

It may be worth while to consider briefly the problem of initial instantaneous sources distributed over the plane ( $\xi=0$ ) in a more general manner. In rectangular coordinates the typical distribution is such that the rate per unit of area is

$$\sigma \cos l\xi \cdot \cos m\eta. \quad . \quad . \quad . \quad (14)$$

If we assume that at  $x, y, z$  and time  $t$   $v$  is proportional to  $\cos lx \cdot \cos my$ , the general differential equation (1) gives

$$\begin{aligned} \frac{dv}{dt} + (l^2 + m^2) v &= \frac{d^2 v}{dz^2}, \\ \text{or} \quad \frac{d}{dt} \left\{ e^{(l^2 + m^2)t} v \right\} &= \frac{d^2}{dz^2} \left\{ e^{(l^2 + m^2)t} v \right\}; \end{aligned}$$

so that, as for conduction in one dimension,

$$v = A \cos lx \cos my e^{-(l^2 + m^2)t} \frac{e^{-z^2/4t}}{\sqrt{t}}, \quad . \quad . \quad (15)$$

and

$$\int_{-\infty}^{+\infty} v dz = 2\sqrt{\pi} \cdot A \cos lx \cos my e^{-(l^2 + m^2)t}.$$

Putting  $t=0$ , and comparing with (14), we see that

$$A = \frac{\sigma}{2\sqrt{\pi}}. \quad . \quad . \quad . \quad (16)$$

By means of (2) the solution at time  $t$  may be built up from (14). In this way, by aid of the well-known integral

$$\int_{-\infty}^{+\infty} e^{-a^2 x^2} \cos 2cx dx = \frac{\sqrt{\pi}}{a} e^{-c^2/a^2}, \quad . \quad . \quad (17)$$

we may obtain (15) independently.

The process is of more interest in its application to

\* Gray and Mathews' Bessel's Functions, p. 78, equation (160). Put  $n=0, \lambda=0$ . See also (31) below.



polar coordinates. If we suppose that  $v$  is proportional to  $\cos n\theta \cdot J_n(kr)$ ,

$$\frac{d^2v}{dr^2} + \frac{1}{r} \frac{dv}{dr} + \frac{1}{r^2} \frac{d^2v}{d\theta^2} = -k^2v, \quad . \quad . \quad . \quad (18)$$

so that (1) gives

$$\frac{dv}{dt} + k^2v = \frac{d^2v}{dz^2}, \quad . \quad . \quad . \quad . \quad (19)$$

and

$$v = A \cos n\theta J_n(kr) e^{-k^2t} \frac{e^{-z^2/4t}}{\sqrt{t}} \quad . \quad . \quad . \quad (20)$$

From (20)

$$\int_{-\infty}^{+\infty} v dz = 2\sqrt{\pi} \cdot A \cos n\theta J_n(kr) e^{-k^2t} \quad . \quad . \quad (21)$$

If the initial distribution on the plane  $z=0$  be per unit area

$$\sigma \cos n\theta J_n(kr), \quad . \quad . \quad . \quad . \quad (22)$$

it follows from (21) that as before

$$A = \frac{\sigma}{2\sqrt{\pi}} \quad . \quad . \quad . \quad . \quad (23)$$

We next proceed to investigate the effect of an instantaneous source distributed over the circle for which

$$\xi=0, \quad \xi=a \cos \phi, \quad \eta=a \sin \phi,$$

the rate per unit length of arc being  $q \cos n\phi$ . From (2) at the point  $x, y, z$

$$v = \int_0^{2\pi} \frac{q \cos n\phi e^{-r^2/4t} a d\phi}{8\pi^{3/2} t^{3/2}}, \quad . \quad . \quad . \quad (24)$$

in which

$$r^2 = (\xi - x)^2 + (\eta - y)^2 + z^2 = a^2 + \rho^2 + z^2 - 2a\rho \cos(\phi - \theta),$$

if  $x = \rho \cos \theta$ ,  $y = \rho \sin \theta$ . The integral that we have to consider may be written

$$\begin{aligned} \int_0^{2\pi} \cos n\phi e^{\rho' \cos(\phi - \theta)} d\phi &= \int \cos n(\theta + \psi) e^{\rho' \cos \psi} d\psi \\ &= \cos n\theta \int \cos n\psi e^{\rho' \cos \psi} d\psi - \sin n\theta \int \sin n\psi e^{\rho' \cos \psi} d\psi, \\ &\quad . \quad . \quad . \quad . \quad (25) \end{aligned}$$

where  $\psi = \phi - \theta$ , and  $\rho' = a\rho/2t$ . In view of the periodic

character of the integrand, the limits may be taken as  $-\pi$  and  $+\pi$ . Accordingly

$$\begin{aligned} \int_{-\pi}^{+\pi} \cos n\psi e^{\rho' \cos \psi} d\psi &= 2 \int_0^{\pi} \cos n\psi e^{\rho' \cos \psi} d\psi, \\ \int_{-\pi}^{+\pi} \sin n\psi e^{\rho' \cos \psi} d\psi &= 0; \quad \text{and} \\ \int_0^{2\pi} \cos n\phi \cdot e^{\rho' \cos(\phi-\theta)} d\phi &= 2 \cos n\theta \int_0^{\pi} \cos n\psi e^{\rho' \cos \psi} d\psi \\ &\quad \dots \dots \dots (26) \end{aligned}$$

The integral on the right of (26) is equivalent to  $\pi I_n(\rho')$ , where

$$i^n I_n(\rho') = J_n(i\rho'), \quad \dots \dots \dots (27)$$

$J_n$  being, as usual, the symbol of Bessel's function of order  $n$ . For, if  $n$  be even,

$$\begin{aligned} \int_0^{\pi} \cos n\psi e^{\rho' \cos \psi} d\psi &= \frac{1}{2} \int_0^{\pi} \cos n\psi (e^{\rho' \cos \psi} + e^{-\rho' \cos \psi}) d\psi \\ &= \int_0^{\pi} \cos n\psi \cos(i\rho' \cos \psi) d\psi = \pi i^{-n} J_n(i\rho') = \pi I_n(\rho'); \end{aligned}$$

and, if  $n$  be odd,

$$\begin{aligned} \int_0^{\pi} \cos n\psi e^{\rho' \cos \psi} d\psi &= -\frac{1}{2} \int_0^{\pi} \cos n\psi (e^{-\rho' \cos \psi} - e^{\rho' \cos \psi}) d\psi \\ &= -i \int_0^{\pi} \cos n\psi \sin(i\rho' \cos \psi) d\psi = \pi I_n(\rho'). \end{aligned}$$

In either case

$$\int_0^{\pi} \cos n\psi e^{\rho' \cos \psi} d\psi = \pi I_n(\rho'). \quad \dots \dots (28)$$

Thus

$$\int_0^{2\pi} \cos n\phi e^{\rho' \cos(\phi-\theta)} d\phi = 2\pi \cos n\theta I_n(\rho'), \quad (29)$$

and (24) becomes

$$v = \frac{qa \cos n\theta}{4\pi^{1/2} t^{3/2}} I_n\left(\frac{a\rho}{2t}\right) e^{-\frac{a^2 + \rho^2 + z^2}{4t}} \dots \dots (30)$$

This gives the temperature at time  $t$  and place  $(\rho, z)$  due to an initial instantaneous source distributed over the circle  $a$ .

The solution (30) may now be used to find the effect of the initial source expressed by (22). For this purpose we

replace  $q$  by  $\sigma da$ , and introduce the additional factor  $J_n(ka)$ , subsequently integrating with respect to  $a$  between the limits 0 and  $\infty$ . Comparing the result with that expressed in (20), (23), we see that

$$\frac{\sigma \cos n\theta e^{-z^2/4t}}{2\sqrt{(\pi t)}}$$

is a common factor which divides out, and that there remains the identity

$$\frac{e^{-\rho^2/4t}}{2t} \int_0^\infty a da e^{-a^2/4t} J_n(ka) I_n\left(\frac{a\rho}{2t}\right) = J_n(k\rho) e^{-k^2t}. \quad (31)$$

This agrees with the formula given by Weber, which thus receives an interesting interpretation.

Reverting to (30), we recognize that it must satisfy the fundamental equation (1), now taking the form

$$\frac{d^2v}{dz^2} + \frac{d^2v}{d\rho^2} + \frac{1}{\rho} \frac{dv}{d\rho} + \frac{1}{\rho^2} \frac{d^2v}{d\theta^2} = \frac{dv}{dt}; \quad (32)$$

and that when  $t=0$   $v$  must vanish, unless also  $z=0$ ,  $\rho=a$ .

If we integrate (30) with respect to  $z$  between  $\pm\infty$ , setting  $q=\sigma dz$ , so that  $\sigma \cos n\theta$  represents the superficial density of the instantaneous source distributed over the cylinder of radius  $a$ , we obtain

$$v = \frac{\sigma a \cos n\theta}{2t} I_n\left(\frac{a\rho}{2t}\right) e^{-\frac{a^2+\rho^2}{4t}}, \quad (33)$$

which may be regarded as a generalization of (9). And it appears that (33) satisfies (32), in which the term  $d^2v/dz^2$  may now be omitted.

In V. Kelvin gives the temperature at a distance  $r$  from the centre and at time  $t$  due to an instantaneous source uniformly distributed over a spherical surface. In deriving the result by integration from (2) it is of course simplest to divide the spherical surface into elementary circles which are symmetrically situated with respect to the line OQ joining the centre of the sphere O to the point Q where the effect is required. But if the circles be drawn round another axis OA, a comparison of results will give a definite integral.

Adapting (12), we write  $a=c \sin \theta$ ,  $c$  being the radius of the sphere,  $x=OQ \sin \theta'=r \sin \theta'$ ,  $z=r \cos \theta'-c \cos \theta$ , so that

$$v = \frac{qc \sin \theta e^{-(c^2+r^2)/4t}}{4\pi^{1/2} t^{3/2}} I_0\left(\frac{cr \sin \theta \sin \theta'}{2t}\right) e^{\frac{rc \cos \theta \cos \theta'}{2t}}. \quad (34)$$

This has now to be integrated with respect to  $\theta$  from 0 to  $\pi$ . Since the result must be independent of  $\theta'$ , we see by putting  $\theta' = 0$  that

$$\begin{aligned} \int_0^\pi I_0 (\rho \sin \theta \sin \theta') e^{\rho \cos \theta \cos \theta'} \sin \theta d\theta \\ = \int_0^\pi e^{\rho \cos \theta} \sin \theta d\theta = \frac{1}{\rho} (e^\rho - e^{-\rho}). \quad . \quad . \quad (35) \end{aligned}$$

Using the simplified form and putting  $q = \sigma c d\theta$ , where  $\sigma$  is the superficial density, we obtain for the complete sphere

$$v = \frac{\sigma c}{2\pi^{\frac{1}{2}} t^{\frac{1}{2}} r} \left( e^{-\frac{(c-r)^2}{4t}} - e^{-\frac{(c+r)^2}{4t}} \right), \quad . \quad . \quad (36)$$

agreeing with (6) when we remember that  $Q = 4\pi c^2 \sigma$ .

We will now consider the problem of an instantaneous source arbitrarily distributed over the surface of the sphere whose radius is  $c$ . It suffices, of course, to treat the case of a spherical harmonic distribution; and we suppose that per unit of area of the spherical surface the rate is  $S_n$ . Assuming that  $v$  is everywhere proportional to  $S_n$ , we know that  $v$  satisfies

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{dv}{d\theta} \right) + \frac{1}{\sin^2 \theta} \frac{d^2 v}{d\omega^2} + n(n+1)v = 0, \quad . \quad (37)$$

$\theta, \omega$  being the usual spherical polar coordinates. Hence from (1)  $v$  as a function of  $r$  and  $t$  satisfies

$$\frac{dv}{dt} = \frac{d^2 v}{dr^2} + \frac{2}{r} \frac{dv}{dr} - \frac{n(n+1)v}{r^2} = 0,$$

or

$$\frac{d(rv)}{dt} = \frac{d^2(rv)}{dr^2} - \frac{n(n+1)}{r^2} (rv) = 0. \quad . \quad . \quad (38)$$

When  $n=0$ , this reduces to the same form as applies in one dimension. For general values of  $n$  the required solution appears to be most easily found indirectly.

Let us suppose that  $S_n$  reduces to Legendre's function  $P_n(\mu)$ , where  $\mu = \cos \theta$ , and let us calculate directly from (2) the value of  $v$  at time  $t$  and at a point Q distant  $r$  from the centre of the sphere along the axis of  $\mu$ . The exponential term is

$$e^{-\frac{r^2+c^2}{4t}} e^{\frac{rc\mu}{2t}} = e^{-\frac{r^2+c^2}{4t}} e^{\rho\mu}, \quad . \quad . \quad . \quad (39)$$

if  $\rho = rc/2t$ . Now ('Theory of Sound,' § 334)

$$\int_{-1}^{+1} P_n(\mu) e^{i\rho\mu} d\mu = 2i^n \sqrt{\left(\frac{\pi}{2\rho}\right)} J_{n+\frac{1}{2}}(\rho), \quad (40)$$

whence

$$\int_{-1}^{+1} P_n(\mu) e^{\rho\mu} d\mu = 2i^{n+\frac{1}{2}} \sqrt{\left(\frac{\pi}{2\rho}\right)} J_{n+\frac{1}{2}}(-i\rho), \quad (41)$$

or, as it may also be written by (27),

$$= 2 \sqrt{\left(\frac{\pi}{2\rho}\right)} I_{n+\frac{1}{2}}(\rho). \quad (42)$$

Substituting in (2)

$$Q = 2\pi c^2 P_n(\mu) d\mu, \quad (43)$$

we now get for the value of  $v$  at time  $t$ , and at the point for which  $\rho = r$ ,  $\mu = 1$ ,

$$rv = \frac{i^{n+\frac{1}{2}} c^{3/2} r^{\frac{1}{2}} e^{-(r^2+c^2)/4t}}{2t} J_{n+\frac{1}{2}}\left(-\frac{irc}{2t}\right). \quad (44)$$

It may be verified by trial that (44) is a solution of (38). When  $\mu$  is not restricted to the value unity, the only change required in (44) is the introduction of the factor  $P_n(\mu)$ .

When  $n=0$ ,  $P_n(\mu)=1$ , and we fall back upon the case of *uniform* distribution. We have

$$J_{\frac{1}{2}}(x) = \sqrt{\left(\frac{2}{\pi x}\right)} \sin x, \quad (45)$$

$$\text{or} \quad J_{\frac{1}{2}}(-ix) = i^{-\frac{1}{2}} \frac{e^x - e^{-x}}{\sqrt{(2\pi x)}}. \quad (46)$$

Using this in (44), we obtain a result in accordance with (6), in which  $Q$ , representing the integrated magnitude of the source, is equal to  $4\pi c^2$  in our present reckoning.

When  $n=1$ ,  $P_1(\mu)=\mu$ , and

$$J_{3/2}(x) = \sqrt{\left(\frac{2}{\pi x}\right)} \left\{ \frac{\sin x}{x} - \cos x \right\}; \quad (47)$$

and whatever integral value  $n$  may assume  $J_{n+\frac{1}{2}}$  is expressible in finite terms.

We have supposed that the rate of distribution is represented by a Legendre's function  $P_n(\mu)$ . In the more general case it is evident that we have merely to multiply the right-hand member of (44) by  $S_n$ , instead of  $P_n$ .

*Phil. Mag.* S. 6. Vol. 22. No. 129. *Sept.* 1911. 2 D

So far we have been considering instantaneous sources. As in II., the effect of *constant* sources may be deduced by integration, although the result is often more readily obtained otherwise. A comparison will, however, give the value of a definite integral. Let us apply this process to (33) representing the effect of a cylindrical source.

The required solution, being independent of  $t$ , is obtained at once from (1). We have inside the cylinder

$$v = A\rho^n \cos n\theta,$$

and outside

$$v = B\rho^{-n} \cos n\theta,$$

with  $Aa^n = Ba^{-n}$ . The intensity of the source is represented by the difference in the values of  $dv/d\rho$  just inside and just outside the cylindrical surface. Thus

$$\sigma' \cos n\theta = n \cos n\theta (Ba^{-n-1} + Aa^{n-1}),$$

whence

$$Aa^n = Ba^{-n} = \sigma'a/2n,$$

$\sigma' \cos n\theta$  being the constant time rate. Accordingly, within the cylinder

$$v = \frac{\sigma'a}{2n} \left(\frac{\rho}{a}\right)^n \cos n\theta, \quad . \quad . \quad . \quad . \quad (48)$$

and without the cylinder

$$v = \frac{\sigma'a}{2n} \left(\frac{\rho}{a}\right)^{-n} \cos n\theta. \quad . \quad . \quad . \quad . \quad (49)$$

These values are applicable when  $n$  is any positive integer. When  $n$  is zero, there is no permanent distribution of temperature possible.

These solutions should coincide with the value obtained from (33) by putting  $\sigma = \sigma' dt$  and integrating with respect to  $t$  from 0 to  $\infty$ . Or

$$\int_0^\infty \frac{dt}{t} I_n\left(\frac{a\rho}{2t}\right) e^{-\frac{a^2+\rho^2}{4t}} = \frac{1}{n} \left(\frac{\rho}{a}\right)^{\pm n}, \quad . \quad . \quad . \quad (50)$$

the  $+$  sign in the ambiguity being taken when  $\rho < a$ , and the  $-$  sign when  $\rho > a$ . I have not confirmed (50) independently.

In like manner we may treat a constant source distributed over a *sphere*. If the rate per unit time and per unit of

area of surface be  $S_n$ , we find, as above, for inside the sphere ( $c$ )

$$v = \frac{c}{2n+1} \left(\frac{r}{c}\right)^n S_n, \quad \dots \quad (51)$$

and outside the sphere

$$v = \frac{c}{2n+1} \left(\frac{c}{r}\right)^{n+1} S_n, \quad \dots \quad (52)$$

and these forms are applicable to any integral  $n$ , zero included. Comparing with (44), we see that

$$i^{n+\frac{1}{2}} \int_0^\infty \frac{dt}{t} e^{-\frac{r^2+c^2}{4t}} J_{n+\frac{1}{2}}\left(-\frac{irc}{2t}\right) = \frac{2}{2n+1} \left(\frac{r}{c}\right)^{\pm(n+\frac{1}{2})}, \quad (53)$$

which does not differ from (50), if in the latter we suppose  $n = \text{integer} + \frac{1}{2}$ .

The solution for a time-periodic simple point-source has already been quoted from Kelvin (IV.). Though derivable as a particular case from (4), it is more readily obtained from the differential equation (1) taking here the form—see (38) with  $n=0$ —

$$\frac{d^2(rv)}{dt} = \frac{d^2(rv)}{dr^2},$$

or if  $v$  is assumed proportional to  $e^{ipt}$ ,

$$d^2(rv)/dr^2 - ip(rv) = 0, \quad \dots \quad (54)$$

giving

$$rv = A e^{ipt} e^{-i^{\frac{1}{2}} p^{\frac{1}{2}} r}, \quad \dots \quad (55)$$

as the symbolical solution applicable to a source situated at  $r=0$ . Denoting by  $q$  the magnitude of the source, as in (5), we get to determine  $A$ ,

$$\left[ -4\pi r^2 \frac{dv}{dr} \right]_{r=0} = q e^{ipt} = 4\pi A,$$

so that

$$v = \frac{q}{4\pi r} e^{ipt} e^{-i^{\frac{1}{2}} p^{\frac{1}{2}} r}. \quad \dots \quad (56)$$

If from (56) we discard the imaginary part, we have

$$v = \frac{q}{4\pi r} e^{-r \sqrt{(p/2)}} \cos \{pt - r \sqrt{(p/2)}\}, \quad \dots \quad (57)$$

corresponding to the source  $q \cos pt$ .

From (56) it is possible to build up by integration solutions relating to various distributions of periodic sources over lines or surfaces, but an independent treatment is usually simpler.

We will, however, write down the integral corresponding to a uniform linear source coincident with the axis of  $z$ . If  $\rho^2 = x^2 + y^2$ ,  $r^2 = z^2 + \rho^2$ , and ( $\rho$  being constant)  $r dr = z dz$ . Thus putting in (56)  $q = q_1 dz$ , we get

$$v = \frac{q_1 e^{ipt}}{2\pi} \int_{\rho}^{\infty} \frac{e^{-r} \sqrt{(ip)} dr}{\sqrt{(r^2 - \rho^2)}} \cdot \cdot \cdot \cdot (58)$$

In considering the effect of periodic sources distributed over a plane  $xy$ , we may suppose

$$v \propto \cos lx \cdot \cos my, \cdot \cdot \cdot \cdot (59)$$

$$\text{or again} \quad v \propto J_n(kr) \cdot \cos n\theta, \cdot \cdot \cdot \cdot (60)$$

where  $r^2 = x^2 + y^2$ . In either case if we write  $l^2 + m^2 = k^2$ , and assume  $v$  proportional to  $e^{ipt}$ , (1) gives

$$d^2v/dz^2 = (k^2 + ip)v. \cdot \cdot \cdot \cdot (61)$$

Thus, if

$$k^2 + ip = R(\cos \alpha + i \sin \alpha), \cdot \cdot \cdot \cdot (62)$$

$$v = A e^{-\sqrt{R} \cdot (\cos \frac{1}{2}\alpha + i \sin \frac{1}{2}\alpha)z} e^{ipt}, \cdot \cdot \cdot \cdot (63)$$

where  $A$  includes the factors (59) or (60). If the value of  $v$  be given on the plane  $z=0$ , that of  $A$  follows at once. If the magnitude of the source be given,  $A$  is to be found from the value of  $dv/dz$  when  $z=0$ .

The simplest case is of course that where  $k=0$ . If  $V e^{ipt}$  be the value of  $v$  when  $z=0$ , we find

$$v = V e^{ipt} e^{-z \sqrt{(ip)}}; \cdot \cdot \cdot \cdot (64)$$

or when realized

$$v = V e^{-z \sqrt{(p/2)}} \cos \{pt - z \sqrt{(p/2)}\}, \cdot \cdot \cdot (65)$$

corresponding to

$$v = V \cos pt \quad \text{when } z=0.$$

From (64)

$$-\left(\frac{dv}{dz}\right)_0 = \sqrt{(ip)} \cdot V e^{ipt} = \frac{1}{2}\sigma e^{ipt}, \cdot \cdot \cdot (66)$$

if  $\sigma$  be the source per unit of area of the plane regarded as operative in a medium indefinitely extended in both directions. Thus in terms of  $\sigma$ ,

$$v = \frac{\sigma}{2\sqrt{p}} e^{i(pt - \frac{1}{4}\pi)} e^{-z \sqrt{(ip)}}, \cdot \cdot \cdot \cdot (67)$$

or in real form

$$v = \frac{\sigma}{2\sqrt{p}} e^{-z \sqrt{(p/2)}} \cos \{pt - \frac{1}{4}\pi - z \sqrt{(p/2)}\}, (68)$$

corresponding to the uniform source  $\sigma \cos pt$ .



In the above formulæ  $z$  is supposed to be positive. On the other side of the source, where  $z$  itself is negative, the signs must be changed so that the terms containing  $z$  may remain negative in character.

When periodic sources are distributed over the surface of a sphere (radius= $c$ ), we may suppose that  $v$  is proportional to the spherical surface harmonic  $S_n$ . As a function of  $r$  and  $t$ ,  $v$  is then subject to (38); and when we introduce the further supposition that as dependent on  $t$ ,  $v$  is proportional to  $e^{ipt}$ , we have

$$\frac{d^2(rv)}{dr^2} - \frac{n(n+1)}{r^2} (rv) - ip (rv) = 0. \quad (69)$$

When  $n=0$ , that is in the case of symmetry round the pole, this equation takes the same form as for one dimension; but we have to distinguish between the inside and the outside of the sphere.

On the inside the constants must be so chosen that  $v$  remains finite at the pole ( $r=0$ ). Hence

$$rv = A e^{ipt} (e^{r \sqrt{ip}} - e^{-r \sqrt{ip}}), \quad (70)$$

or in real form

$$\begin{aligned} rv &= A e^{r \sqrt{p/2}} \cos \{pt + r \sqrt{p/2}\} \\ &- A e^{-r \sqrt{p/2}} \cos \{pt - r \sqrt{p/2}\}. \end{aligned} \quad (71)$$

Outside the sphere the condition is that  $rv$  must vanish at infinity. In this case

$$rv = B e^{ipt} e^{-r \sqrt{ip}}, \quad (72)$$

or in real form

$$rv = B e^{-r \sqrt{p/2}} \cos \{pt - r \sqrt{p/2}\}. \quad (73)$$

When  $n$  is not zero, the solution of (69) may be obtained as in Stokes's treatment of the corresponding acoustical problem ('Theory of Sound,' ch. xvii.). Writing  $r \sqrt{ip} = z$ , and assuming

$$rv = A e^z + B e^{-z}, \quad (74)$$

where  $A$  and  $B$  are functions of  $z$ , we find for  $B$

$$\frac{d^2 B}{dz^2} - 2 \frac{dB}{dz} - \frac{n(n+1)}{z^2} B = 0. \quad (75)$$

The solution is

$$B = B_0 f_n(z), \quad . \quad . \quad . \quad . \quad . \quad (76)$$

where  $B_0$  is independent of  $z$  and

$$f_n(z) = 1 + \frac{n(n+1)}{2 \cdot z} + \frac{(n-1)n(n+1)(n+2)}{2 \cdot 4 \cdot z^2} + \dots, \quad (77)$$

as may be verified by substitution. Since  $n$  is supposed integral, the series (77) terminates. For example, if  $n=1$ , it reduces to the first two terms.

The solution appropriate to the exterior is thus

$$rv = B_0 S_n e^{ipt} e^{-r \sqrt{(ip)}} f_n(i^{\frac{1}{2}} p^{\frac{1}{2}} r). \quad . \quad . \quad . \quad (78)$$

For the interior we have

$$rv = A_0 S_n e^{ipt} \{e^{-r \sqrt{(ip)}} f_n(i^{\frac{1}{2}} p^{\frac{1}{2}} r) - e^{r \sqrt{(ip)}} f_n(-i^{\frac{1}{2}} p^{\frac{1}{2}} r)\}, \quad (79)$$

which may also be expressed by a Bessel's function of order  $n + \frac{1}{2}$ .

In like manner we may treat the problem in two dimensions, where everything may be expressed by the polar coordinates  $r, \theta$ . It suffices to consider the terms in  $\cos n\theta$ , where  $n$  is an integer. The differential equation analogous to (69) is now

$$\frac{d^2 v}{dr^2} + \frac{1}{r} \frac{dv}{dr} - \frac{n^2}{r^2} v = ip v, \quad . \quad . \quad . \quad (80)$$

which, if we take  $r\sqrt{(ip)} = z$ , as before, may be written

$$\frac{d^2(z^{\frac{1}{2}}v)}{dz^2} - \frac{(n-\frac{1}{2})(n+\frac{1}{2})}{z^2} (z^{\frac{1}{2}}v) = z^{\frac{1}{2}}v, \quad . \quad . \quad (81)$$

and is of the same form as (69) when in the latter  $n - \frac{1}{2}$  is written for  $n$ .

As appears at once from (80), the solution for the interior of the cylinder may be expressed

$$v = A \cos n\theta e^{ipt} J_n(i^{3/2} p^{1/2} r), \quad . \quad . \quad . \quad (82)$$

$J_n$  being as usual the Bessel's function of the  $n$ th order.

For the exterior we have from (81)

$$r^{\frac{1}{2}}v = B \cos n\theta e^{ipt} e^{-r \sqrt{(ip)}} f_{n-\frac{1}{2}}(i^{\frac{1}{2}} p^{\frac{1}{2}} r), \quad . \quad . \quad (83)$$

where

$$\begin{aligned} f_{n-\frac{1}{2}}(z) = & 1 + \frac{4n^2-1^2}{1 \cdot 8z} + \frac{(4n^2-1)(4n^2-3^2)}{1 \cdot 2 \cdot (8z)^2} \\ & + \frac{(4n^2-1^2)(4n^2-3^2)(4n^2-5^2)}{1 \cdot 2 \cdot 3 \cdot (8z)^3} + \dots \end{aligned} \quad (84)$$

The series (84), unlike (77), does not terminate. It is ultimately divergent, but may be employed for computation when  $z$  is moderately great.

In these periodic solutions the sources distributed over the plane, sphere, or cylinder are supposed to have been in operation for so long a time that any antecedent distribution of temperature throughout the medium is without influence. By Fourier's theorem this procedure may be generalized. Whatever be the character of the sources with respect to time, it may be resolved into simple periodic terms; and if the character be known through the whole of past time, the solution so obtained is unambiguous. The same conclusion follows if, instead of the magnitude of the sources, the temperature at the surfaces in question be known through past time.

An important particular case is when the character of the function is such that the superficial value, having been constant (zero) for an infinite time, is suddenly raised to another value, say unity, and so maintained. The Fourier expression for such a function is

$$\frac{1}{2} + \frac{1}{\pi} \int_0^\infty \frac{\sin pt}{p} dp, \quad . . . . (85)$$

the definite integral being independent of the arithmetical value of  $t$ , but changing sign when  $t$  passes through 0; or, on the understanding that only the real part is to be retained,

$$\frac{1}{2} + \frac{1}{i\pi} \int_0^\infty \frac{e^{ipt}}{p} dp. \quad . . . . (86)$$

We may apply this at once to the case of the plane  $z=0$  which has been at 0 temperature from  $t=-\infty$  to  $t=0$ , and at temperature 1 from  $t=0$  to  $t=\infty$ . By (64)

$$v = \frac{1}{2} + \frac{1}{i\pi} \int_0^\infty \frac{e^{ipt-z\sqrt{(ip)}}}{p} dp. \quad . . . (87)$$

By the methods of complex integration this solution may be transformed into Fourier's, viz.

$$\frac{dv}{dz} = - \frac{1}{\sqrt{(\pi t)}} e^{-z^2/4t}, \quad . . . . (88)$$

$$v = 1 - \frac{2}{\sqrt{\pi}} \int_0^{z/2\sqrt{t}} e^{-\alpha^2} d\alpha, \quad . . . (89)$$

which are, however, more readily obtained otherwise.

In the case of a cylinder ( $r=c$ ) whose surface has been at 0 up to  $t=0$  and afterwards at  $t=1$ , we have from (83) with  $n=0$

$$v = \frac{1}{2} + \frac{c^{\frac{1}{2}}}{i\pi r^{\frac{1}{2}}} \int_0^{\infty} e^{ipt + (c-r)\sqrt{(ip)}} \frac{f_{-\frac{1}{2}}(i^{\frac{1}{2}} p^{\frac{1}{2}} r)}{f_{-\frac{1}{2}}(i^{\frac{1}{2}} p^{\frac{1}{2}} c)} \frac{dp}{p}, \quad (90)$$

of which only the real part is to be retained. This applies to the region outside the cylinder.

It may be observed that when  $t$  is negative (87) must vanish for positive  $z$  and (90) for  $r > c$ .

July 19, Terling Place, Witham, Essex.

### XXXIX. *The Spectra of the Fluorescent Röntgen Radiations.*

By CHARLES G. BARKLA, M.A., D.Sc., *Wheatstone Professor of Physics, University of London, King's College* \*.

THOUGH the properties of the fluorescent X-radiations, emitted by various substances during exposure to X-rays, have been dealt with in a number of papers and notes by the writer †, the accounts have been neither complete nor connected. The purpose of the present paper is to present the subject as it stands at the time of writing, without entering into details of experiments. This seems almost a necessity in indicating lines of future research, and in showing the true simplicity of what appear at first sight to be very complex phenomena.

When substances are exposed to Röntgen radiation they emit X-radiations of two distinct types. One of these radiations, like the primary in penetrating power and general properties, has been termed the scattered radiation, being analogous to light scattered from small particles. The other, a completely transformed X-radiation has been termed the characteristic secondary X-radiation, the homogeneous secondary X-radiation, and latterly the fluorescent X-radiation, on account of its similarity to fluorescent light.

The scattered radiation has been fully dealt with by the writer ‡, but it is necessary here to note its characteristics in

\* Communicated by the Author. The expenses of these researches have been partially covered by a Government Grant through the Royal Society.

† Barkla, *Phil. Mag.* June 1906, Feb. 1908, Oct. 1910; *Proc. Camb. Phil. Soc.* May 1909; *Jahrbuch der Radioaktivität*, iii. pp. 246-324. Barkla and Sadler, *Phil. Mag.* Sept. 1907, Oct. 1908, May 1909. Barkla and Ayres, *Phil. Mag.* Feb. 1911.

‡ *Phil. Mag.* June 1903, May 1904, Feb. 1908, Feb. 1911; *Phil. Trans. A.* vol. cciv. 1905, pp. 467-479; *Proc. Roy. Soc. A.* vol. lxxvii. 1906, pp. 247-255.

order to distinguish it from the fluorescent radiation. Observation of radiation of this type has been possible owing to the fact that the lightest elements—from hydrogen to sulphur—when subject to a beam of X-rays of ordinary penetrating power, emit X-radiation which at a distance of several centimetres in air is almost entirely, if not entirely, a scattered radiation. If these elements emit fluorescent X-radiations under such conditions, they are either absorbed in a very thin layer of air and do not reach the electroscope, or are so penetrating as to produce no appreciable ionization in the electroscope. The former appears probable, the latter highly improbable, as will subsequently be seen.

The scattered radiation is indistinguishable in most of its properties from the primary radiation producing it. It has the same penetrating power as the primary. When slight differences are observed these differences are most marked when the experimental conditions are such as to introduce a quantity of the fluorescent radiation, that is when more penetrating primary beams are used. In experiments with only moderately penetrating rays, the primary and secondary beams are indistinguishable as regards penetrating power. It has yet to be proved that a secondary X-radiation which does not contain some fluorescent X-radiation differs in penetrating power from the primary radiation producing it.

As the ordinary primary beam is extremely heterogeneous, as shown by successive absorptions by similar plates of any material, the similarity in character of the scattered radiation is evidence of the equality of scattering of the various constituents, that is the various constituents appear in the secondary beam in the same proportion as in the primary. It is also seen by direct experiment that X-rays varying considerably in penetrating power are scattered to the same extent in passing through a given quantity of matter. A limit to this law has not been found, though the range of penetrating power might be considerably extended.

The scattered radiation proceeding in a direction perpendicular to that of propagation of the original primary radiation is very fully polarized, and in the same manner as light scattered from small particles.

The scattered radiation is not equally intense in all directions around the primary beam, but exhibits a slight polarity of the primary such as would be expected on the electromagnetic theory of the production of X-rays.

The writer found the polarization to diminish with an increase in the penetrating power of the radiation from the bulb, whereas with the bulb in a given state the more

penetrating portion of the primary beam exhibited greater polarization than the more absorbable portion. These results may be explained from a consideration of the origin of primary and secondary rays in the anticathode of an X-ray tube. Sufficient experiments have, however, not been made to permit one to say whether these results are perfectly general or not.

The distribution of the scattered radiation in a plane containing the direction of propagation of the primary beam agrees remarkably well with the theoretical distribution within wide limits. The intensity  $I_\theta$  in any direction making an angle  $\theta$  with the direction of propagation of the primary beam is given by  $I_\theta = I_\pi \frac{1}{2} (1 + \cos^2 \theta)$ . There is, however, a

large discrepancy between the theoretical and experimental values when  $\theta$  is less than  $30^\circ$ . From the accuracy of the agreement for all other values of  $\theta$ , it may be concluded that this discrepancy is due to some special conditions in directions near to that of propagation of the primary beam. Further experiments are at present being made to determine these. It is unnecessary at this stage to consider various hypotheses in explanation of the experimental result.

The total fraction of the energy of primary radiation which is scattered depends on both the penetrating power of the primary radiation and on the particular substance traversed by the primary beam. The elements from hydrogen to sulphur scatter the same amount mass for mass; that is when a given beam passes through sulphur and oxygen say, the scattering is twice as great per atom of sulphur as per atom of oxygen. From heavier elements it appears that the scattering is greater mass for mass than from light elements. From copper, for instance, after the fluorescent radiation had been absorbed there remained twice as much radiation, presumably scattered radiation, as from an equal mass of the light elements. From silver, too, a radiation showing practically full polarization effects, and therefore a scattered radiation, was of the order of six times the intensity of that from the light elements. These results may only be taken as giving the order of magnitude of the relative intensities. Further work on other elements under exposure to various primary beams is needed.

The fluorescent X-radiations emitted by elements exposed to an ordinary beam of X-rays have been described in early papers by the writer and Dr. Sadler as homogeneous secondary X-radiations, or as characteristic secondary X-radiations.

The term fluorescent radiation seems, however, preferable to either of the others. Radiation of this type may very readily be observed from elements of higher atomic weight than sulphur, when the observing electroscope is at a distance of several centimetres from the substance exposed to the primary rays. In most cases, unless special precautions are taken, the ionizing effect of these radiations from any particular element is very much greater than that of the scattered X-rays—indeed it completely swamps the effect of the latter. But, as will be seen later, the scattered radiation may be isolated by using a primary beam which is incapable of exciting this fluorescent X-radiation.

In many cases the radiation which reaches an electroscope situated several centimetres from the radiating element is an almost perfectly homogeneous radiation. It is important to point out that though very careful experiments have been made to test this, both directly and indirectly, there is no evidence of the slightest deviation from homogeneity of the fluorescent radiations. There is not only no evidence of lack of homogeneity, but striking evidence of homogeneity. Perfect homogeneity is, of course, not to be expected in these radiations any more than in light, for instance, but for all practical purposes we may assume the radiations accurately homogeneous. The reasons for regarding the radiations as homogeneous will, however, be given.

The direct experiment of successively placing thin sheets of aluminium or other absorbing substance in the path of the radiation and observing the absorptions produced, shows that whereas the fractional diminution in the ionization produced by an ordinary primary beam becomes less and less as plate after plate of absorbing substance is placed in its path—owing to the more absorbable constituents being absorbed by the earlier plates—the fractional diminution of the ionization produced by a secondary beam does not vary after partial absorption. This was shown by Barkla and Sadler (*Phil. Mag.* Oct. 1908) and need not be repeated here. The very slight deviation from homogeneity which is observed after a considerable portion of the radiation has been absorbed is such as would be produced by the superposition of a small amount of scattered radiation. This scattered radiation in some cases produced no more than half of one per cent. of the ionization produced by the homogeneous radiation. The proportion of scattered to fluorescent radiation depends, however, upon the particular primary beam used. The radiations from elements of atomic weights in the neighbourhood of iron, copper, zinc, &c., when subject to a radiation

of ordinary penetrating power, are the most homogeneous, that is contain the smallest proportion of scattered radiation. It was found that the amount of scattered radiation necessary to produce the heterogeneity observed in the radiation from copper was twice that which would be given by an equal mass of the light elements H to S. Even with this admixture of scattered radiation the total radiation was strikingly homogeneous, as shown by fig. 1 in the paper referred to above. It is necessary to absorb an amount somewhere about 95 per cent. of the fluorescent radiation before the effect of the scattered radiation becomes evident.

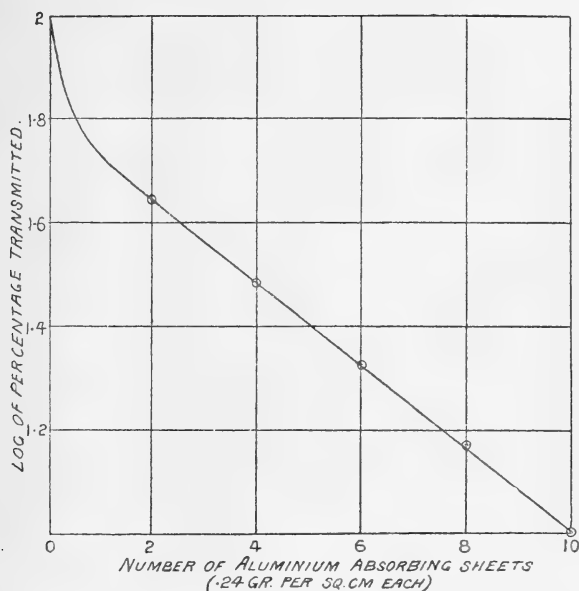
In the radiation emitted under exposure to an ordinary primary beam by elements of atomic weight in the neighbourhood of Ag, Sn, Sb, ... Ce, there are two homogeneous radiations superposed in addition to the scattered radiation—which is more intense than from an equal mass of the light elements. Special precautions have thus to be taken to obtain homogeneous beams from these. Owing to the wide difference in penetrating power between these two principal constituents and to variations in their proportion when excited by a variable primary, the secondary radiation appears heterogeneous, and much more variable in penetrating power than the primary. A small change in the penetrating power of the primary frequently produces very much greater changes in the character of the secondary radiation. This is easily understood from the relation given later between the penetrating power of the primary radiation and the intensity of the secondary radiation which it excites. The homogeneity of the more penetrating fluorescent radiation from barium is shown in fig. 1, in which the logarithm of the fraction transmitted through various sheets of aluminium is plotted against the number of those sheets. The initial drop is due to the easily absorbed constituent; the linear portion exhibits the homogeneity of the more penetrating fluorescent radiation. The homogeneity of the more absorbable constituent was observed by Barkla and Nicol by using a very soft primary beam. This method will be understood from what follows.

The radiations which have been observed from the elements W, Pt, Au, Pb, Bi when these are exposed to primary radiations of ordinary penetrating power are not so homogeneous as the radiations from Fe, Cu, Zn, &c. Slight variations in penetrating power may also be observed when much more considerable variations take place in the primary. Whether there is appreciable heterogeneity in the true fluorescent radiations from these elements or not has not been very



accurately tested. It appears probable that the radiation from these elements contains a greater proportion of scattered radiation. There is also the possibility of the superposition of a small quantity of a second more penetrating fluorescent

Fig. 1.



radiation. The full analysis of these radiations when excited by homogeneous primary radiations would lead to more accurate conclusions. Experiments on the resultant secondary radiation show, however, that these radiations are very homogeneous in comparison with any ordinary primary beam. The fluorescent radiations are thus at any rate approximately homogeneous, and in the absence of more exact evidence will be considered homogeneous, like those radiations upon which more accurate experiments have hitherto been possible.

Indirect evidence that the fluorescent radiations are approximately homogeneous has also been obtained by Barkla and Collier in studying the relation between the absorption of homogeneous X-rays in platinum and gold and the absorption of these rays in aluminium. The curves showing the relation exhibit similar characteristics to those obtained from

experiments on absorption by elements Fe, Cu, &c., which do emit homogeneous fluorescent radiations. (See fig. 2.)

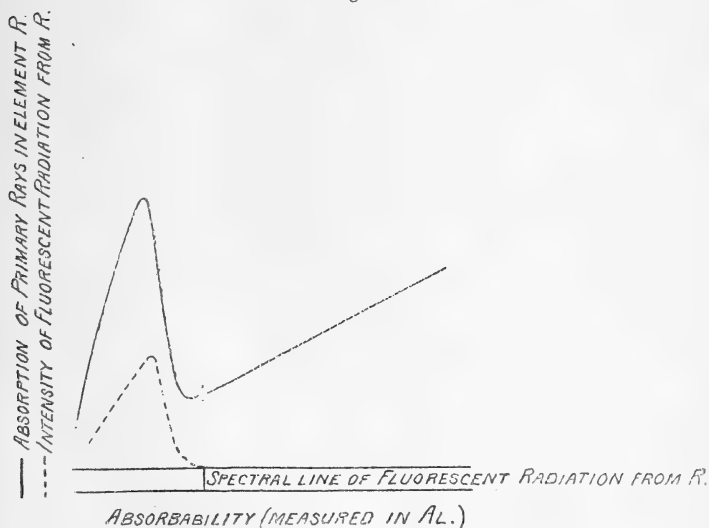
One of the most interesting facts concerning each of these homogeneous fluorescent X radiations is that it is not excited by radiation of lower penetrating power. [The penetrating power must be measured in some substance whose characteristic radiations are not within the range of penetrating power experimented upon, and not near to this range on its more absorbable side.] This was first shown by Barkla and Sadler in the case of the secondary radiation from silver. When a heterogeneous primary beam was used it was frequently found that the homogeneous fluorescent radiation from silver was more penetrating than the primary as a whole; but however absorbable the primary beam was, a plate of aluminium placed in that primary beam diminished the intensity of fluorescent radiation less than the same plate placed so as to intercept the secondary radiation itself, showing that the secondary beam was more absorbable than the portion of the primary beam producing it. Again, in transmitting the homogeneous radiation from copper through iron, it was found that a certain transformation had taken place in the transmitted radiation, due to the excitation in iron of its slightly softer characteristic radiation and the superposition of this on the truly transmitted radiation; whereas when iron radiation was transmitted through copper, that is a very soft radiation through a substance whose characteristic fluorescent X-radiation is of slightly more penetrating type, the radiation emerging was purely iron radiation without the admixture of radiation characteristic of copper. Similar experiments were performed with copper and zinc. The radiation from zinc being slightly more penetrating than that from copper excited in copper its fluorescent radiation, but the process could not be reversed. Dr. Sadler later verified the law with considerable accuracy for a number of radiators, by using homogeneous radiations to excite the fluorescent radiation. All experiments have only further shown the generality and the accuracy of this law, which is analogous to Stokes's law of light fluorescence.

Not only is there this direct evidence, but a considerable amount of indirect evidence obtained from observation of the relation between the absorption in a given substance of X-rays, and their absorption in aluminium, say; also from the relation between ionization produced in different gases by rays of varying penetrating power.

To take the phenomenon of absorption first, it has been shown by the writer and Dr. Sadler that the general variation

in the absorption of X-rays with variation of penetrating power is determined solely by the fluorescent or characteristic radiation of the absorbing substance. Thus as the general absorbability of a radiation decreases—that is as its penetrating power increases—it becomes less and less absorbed in a substance R, say, its absorption being approximately proportional to its absorption in any other substance when the radiations used are not near on the more penetrating side of the radiation characteristic of this second substance. This approximate proportionality holds until the radiation absorbed becomes just more penetrating than the fluorescent radiation characteristic of R. Then as the radiation becomes more penetrating it is absorbed more in R than would be given by this law, the additional absorption being accompanied by the emission of fluorescent radiation from R, by an increased corpuscular radiation from R, and if R is in a gaseous state by an additional ionization in R. The relation between the absorption in R and in any other substance whose characteristic radiations are not near on the more absorbable side to the radiations experimented upon is shown in fig. 2.

Fig 2.



The special point to be observed is the accuracy of this relation in all cases experimented upon. The simple law of approximate proportionality is obeyed until the absorbability of the primary radiation is *just* that of the radiation characteristic of the absorbing substance ; the slightest increase in

penetrating power of the primary is accompanied by a special absorption connected with the emission of fluorescent radiation. The emission of fluorescent radiation implies the special absorption of the primary radiation, and *vice versa*. The absorption curves published by Barkla and Sadler\*, drawn from the results of experiments on absorption by metal sheets, thus indirectly exhibit the accuracy of this law of fluorescence. Similar curves have been got by Barkla and Collier from experiments on absorption by gases and vapours, and with fewer observations near the critical point in the case of absorption by gold and platinum, so that the generality of the law has been well tested.

Similar relations hold between the ionization in R when in the gaseous state and the ionization in another gas or vapour whose fluorescent radiation is not near the range of penetrating power experimented upon on its more absorbable side. The writer showed this in a paper on "Phenomena of X-ray Transmission"†, and later published the relation in detail in the case of ionization in ethyl bromide. A similar relation holds in the case of every gas upon which experiments have been made.

Now the definiteness of the turning point in these absorption and ionization curves, and the coincidence of this penetrating power with that of the fluorescent radiation characteristic of the absorbing and ionized substance is further evidence not only of the homogeneity of the fluorescent radiations, but of the accuracy of the law of X-ray fluorescence analogous to Stokes's law.

Unlike the scattered radiation the fluorescent radiation is uniformly distributed around a polarized beam of X-rays‡. It is also uniformly distributed in a plane containing the direction of propagation of the primary radiation§. Thus the intensity is entirely independent of the direction of electric force or of propagation of the exciting primary beam.

The total energy of the secondary fluorescent radiation is in some cases certainly very great. The variation of intensity with the penetrating power of the primary is shown by the curve in fig. 2||, and at its maximum the copper radiation carries away—if we measure energy by total ionizing power

\* Phil. Mag. May 1909.

† Proc. Camb. Phil. Soc. May 1909.

‡ Phil. Trans. A. vol. cciv. 1905, pp. 467–479; Proc. Roy. Soc. A. vol. lxxvii. 1906, pp. 247–255.

§ Phil. Mag. Feb. 1911.

|| Fig. 2 was given by Barkla and Sadler in a paper on "Absorption of Röntgen Rays" (Phil. Mag. May 1909).

—about  $\frac{1}{3}$  of the energy of the primary beam absorbed, and quite 100 times the energy of the scattered radiation.

The isolation of any particular fluorescent radiation may usually be effected very simply. If it is a fairly penetrating radiation such as that from tin which it is wished to study, then a primary beam should be used with a fair proportion of constituents of more penetrating type. This, as shown, excites the desired radiation and all softer radiations characteristic of the particular substance. But as all the characteristic radiations of a particular element appear to be widely different in penetrating power, the softer constituents may be absorbed by a sheet of aluminium without diminishing to any considerable extent the intensity of the particular radiation studied. Thus, as shown by the absorption curve fig. 1, after the first absorbing plate the remaining radiation was homo-

geneous and of absorptibility given by  $\frac{\lambda}{\rho} = \cdot 8$ . The preliminary filtering out of the easily absorbed constituents is frequently effected by the surface layers of the radiator itself, and by the air separating it from the detecting electroscop.

In order to obtain a very soft fluorescent radiation, such as that from tin, antimony, &c., a very soft X-ray tube should be used to give the primary radiation. This is then not sufficiently penetrating to excite the more penetrating fluorescent radiation, and provided the testing electroscop is placed near to the radiator the more absorbable fluorescent radiation may be readily studied. This radiation is, however, usually mixed with a large quantity of more penetrating scattered radiation. The quantity of this may be estimated by finding how much is transmitted through sheets of aluminium of sufficient thickness to completely absorb the soft fluorescent radiation. By comparison of this with the intensity of radiation transmitted through similar plates of aluminium from a substance such as carbon giving only scattered radiation, the intensity of scattered radiation superposed on the soft fluorescent radiation, and passing through any number of absorbing plates, may be got by proportion from the corresponding intensity from carbon.

After subtraction of the ionization due to the scattered radiation, it is found that the successive sheets by absorption diminish the effect of the radiation transmitted by the same fraction, showing the homogeneity of the soft characteristic radiation (Barkla and Nicol, 'Nature,' Aug. 4, 1910).

*Phil. Mag. S. 6. Vol. 22. No. 129. Sept. 1911. 2 E*

Dealing with the various elements in this way, a large number of fluorescent radiations have been identified. As we have no method of determining the wave-length of the radiation with which we deal, it is necessary to classify the various X-radiations by their absorption in some standard substance. This is not always a complete definition of an X-radiation, for, as has been shown, radiations of three different penetrating powers are absorbed to the same extent in copper, or in iron, or in zinc, &c. This is analogous to saying that refrangibility of light in one substance does not always completely define the light. But just as the refrangibility of light in a substance whose absorption bands are far removed from the radiation used is a sufficient measure of the character of the radiation, so the absorption in aluminium is sufficient to define the Röntgen radiation used, for aluminium does not emit a characteristic fluorescent radiation within the range of penetrating power here dealt with, nor near to it on its more absorbable side. In the following table, column 3 gives the absorbability of the fluorescent radiations as measured in aluminium. The quantity tabulated is  $\lambda/\rho$ , where  $\lambda$  is defined by the equation  $I=I_0 e^{-\lambda x}$  representing the intensity of radiation transmitted through aluminium sheets of density  $\rho$ .

In a number of cases the characteristic radiations from elements were obtained by using compounds containing the elements in combination with light atoms. The only effect of these light atoms was then to add a little scattered radiation to the fluorescent radiation which it was desired to study. The effect of this was, however, negligible. The radiations from Br, Sr, Rb, I, Ba, and Ce were obtained from the compounds bromal hydrate, strontium hydroxide, rubidium carbonate, iodoform, barium hydroxide, and cerium oxide.

It is seen that the radiations fall into two distinct series, here denoted by the letters K and L\*. Though only these two have so far been found, it seems highly improbable that these, consisting of radiations of penetrating power most easily experimented upon, include all fluorescent radiations actually emitted by elements. In support of this we will look first at the phenomena of absorption. As shown in fig. 2, the absorption in a substance R of rays softer than

\* Previously denoted by letters B and A (Proc. Camb. Phil. Soc. May 1909). The letters K and L are, however, preferable, as it is highly probable that series of radiations both more absorbable and more penetrating exist.

TABLE.

Radiator.	Atomic Weight.	Absorbability of Fluorescent Radiation $\left(\frac{\lambda}{\rho} \text{ in Al}\right)$ .		Remarks.
		Series K.	Series L.	
H-Mg ...	1·008—24·32	...	...	No radiation observed: probably very absorbable.
Al .....	27·1	...	...	} Effects of fluorescent radiation observed: measurements not made.
S .....	32·07	...	...	
Ca .....	40·09	435	...	Not so accurate as values below.
Cr .....	52	136	...	} Easily observed and homogeneity proved with considerable accuracy.
Fe .....	55·85	88·5	...	
Co .....	58·97	71·6	...	}
Ni .....	58·68 (61·3)	59·1	...	
Cu .....	63·57	47·7	...	For atomic weight of Ni see paper by Barkla & Sadler (Phil. Mag. Sept. 1907).
Zn .....	65·37	39·4	...	}
As .....	74·96	22·5	...	
Se .....	79·2	18·9	...	}
Br .....	79·92	16·4	...	
Rb .....	85·45	13·7	...	} Not accurately determined for Rb.
Sr .....	87·62	9·4	...	
Mo .....	96·0	4·7	...	}
Rh .....	102·9	3·1	...	
Ag .....	107·88	2·5	700	} Owing to two fluorescent radiations total radiation appears very variable in experiments with primary radiation of ordinary penetrating power.
Su .....	119·0	1·57	...	
Sb .....	120·2	1·21	435	} Series L not obtained with accuracy of series K.
I .....	126·92	·92	306	
Ba .....	137·37	·8	224	}
Ce .....	140·25	·6	...	
W .....	184·0	...	33	} Homogeneity not shown with accuracy, consequently values of absorbability only approximate,
Pt .....	195·0	...	27·5	
Au .....	197·2	...	25	} —possibly rather high.
Pb .....	207·1	...	20	
Bi .....	208	...	19	

*Note.*—Radiations from Cr, Fe, Co, Ni, Cu, Zn, As, Se, Ag were obtained by Barkla and Sadler (Phil. Mag. May 1909); from Mo and Rh by Sadler (Phil. Mag. March 1910); from Ca, Sb, I, Ba Ag<sub>L</sub> by Barkla and Nicol ('Nature,' Aug. 4, 1910); from Br by Chapman.

the softest known fluorescent radiation characteristic of R is approximately proportional to the absorption in aluminium. With rays of higher penetrating power than that of the fluorescent radiation of R, there is a regular deviation from this proportionality, and when the penetrating power is far removed from that of the fluorescent radiation there is again approximation to proportionality to the absorption in aluminium.

This recurrence of the proportionality suggests the possibility, indeed the probability, of similar relations with rays of penetrating power in the neighbourhood of that of a softer fluorescent radiation not yet discovered. This argument might have been applied to indicate the probability of a radiation belonging to series L, when only that of series K was known. It is equally applicable in indicating the probability of a radiation belonging to an undiscovered series M, consisting of still softer radiations, for the same features as those described are shown by the absorption curves for gold and platinum over a range of penetrating power including that of the fluorescent radiation of series L. These absorption curves thus suggest the existence of a more absorbable fluorescent radiation from gold and platinum than that of series L. From the similarity of the behaviour of all the elements we must then admit the probability of the existence of a series M, and the possibility of further series M, N, &c.

Again, the writer has shown the connexion which exists between absorption, secondary radiation, and ionization. The emission of fluorescent radiation from a substance traversed by a primary beam of X-rays is invariably accompanied by a special absorption of the primary rays, and when the substance is in the gaseous state by a special ionization of that substance. It is natural to connect the absorption of *soft* primary beams and the ionization produced by these in passing through matter with the emission of an undetected softer fluorescent X-radiation of series M.

The extreme variation in the penetrating power of the fluorescent radiations thus far observed is enormous, the K radiation from cerium being more than a thousand times as penetrating as the L radiation from silver. The determination of more penetrating radiation than that from cerium and of more absorbable radiation than that from silver has, however, been limited solely by the unsuitability of the methods hitherto employed. It will probably be an easy matter by modification of these methods to considerably extend the number of radiations in these two series.



It is important to notice that there is no evidence of any abrupt change in the character of the radiation with a change in the atomic weight of the radiating substance. It would, for instance, not be surprising to find groupings of the elements similar to those based on chemical properties. No indication of anything of the sort has been obtained.

In early papers the elements were for convenience divided into groups according to the characteristics of the radiation they emitted when exposed to primary beams of ordinary penetrating power. The elements of different groups appeared at first sight to be fundamentally different in their behaviour, but it was later shown by the writer that the behaviour of one element is typical of all. The observed differences were due simply to wide differences in the relation between the penetrating power of the primary radiation and the fluorescent radiations.

An increase in the atomic weight of an element is invariably accompanied by an increase in the penetrating power of the fluorescent radiation of the same series. This is not always apparent without analysis of the radiations owing to differences in the relative proportions of the fluorescent radiations from various elements under exposure to the same primary radiation. The relation between the atomic weight of an element and the absorbability (as measured by the absorption in aluminium) of its fluorescent X-radiations is shown in fig. 3 (p. 410). The range of absorbability is, however, too great to admit of accurate representation of the relative absorptions of the most penetrating radiations. A more convenient method of exhibiting the relation throughout the entire range is that of plotting the logarithm of the absorbability against atomic weight of the radiator, absorbability being  $\lambda/\rho$ , where  $\lambda$  is given by the equation  $I = I_0 e^{-\lambda x}$ , representing transmission through aluminium of density  $\rho$  (fig. 4, p. 411).

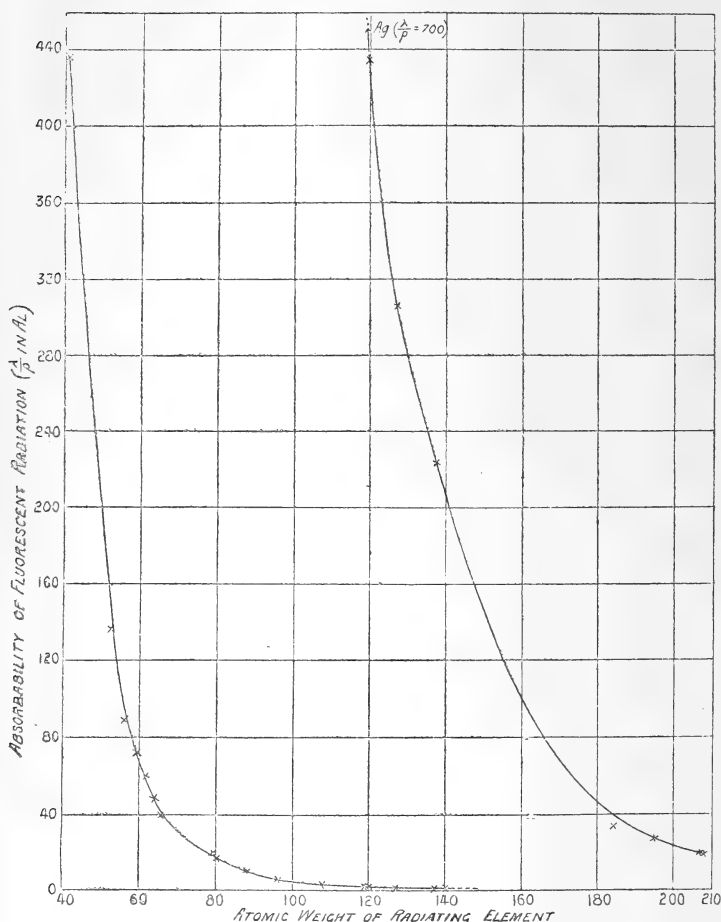
It will be observed that for each series the value of  $\log \lambda/\rho$  is approximately a linear function of the atomic weight of the radiating element. It is remarkable that this should hold closely over such a range in penetrating power.

As all the principal phenomena connected with the transmission of X-rays through matter—absorption, ionization, secondary radiation—are determined by the character of the fluorescent radiations characteristic of the elements constituting the matter traversed\*, it is essential to a complete

\* Proc. Camb. Phil. Soc. May 1909.

understanding of these phenomena to be acquainted with the penetrating powers of these fluorescent radiations.

Fig. 3.



It has been shown that each element has its own characteristic fluorescent line spectrum in X-rays. This is very conveniently represented as is a spectrum of ordinary light, except that without a knowledge of the wave-length we are

obliged to define the radiations by their absorption in some standard substance. Thus we may represent the known

Fig. 4.

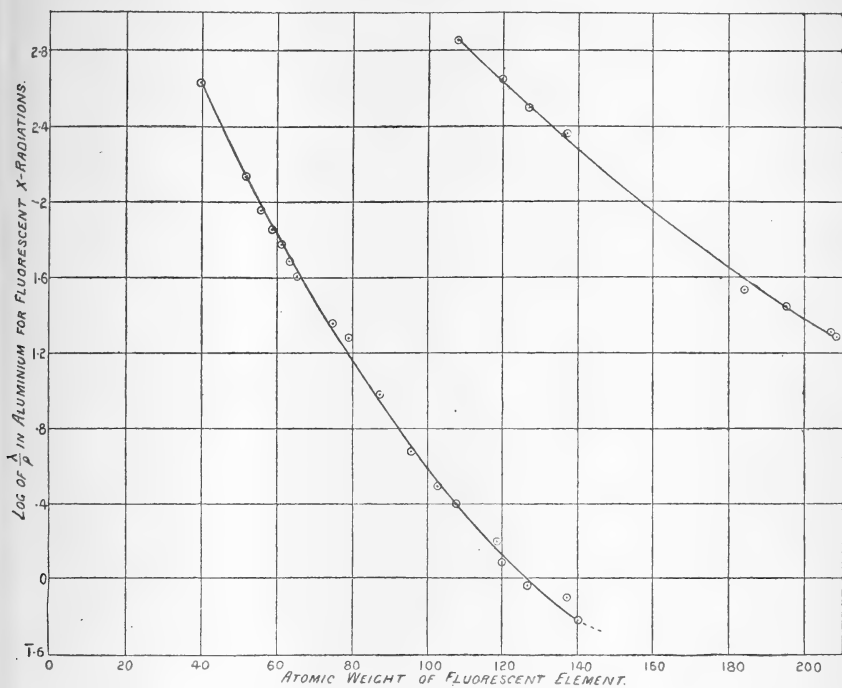
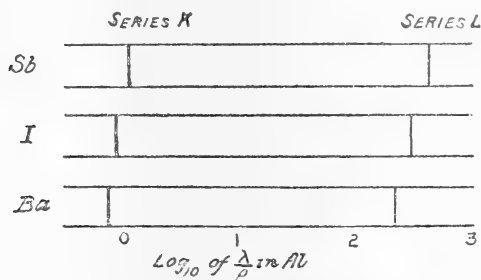


Fig. 5.



portion of the spectra of elements Sb, I, and Ba as in fig. 5. The lines move towards the more penetrating end of the spectrum with an increase in the atomic weight of the element.

It is scarcely too much to say that all the phenomena connected with the transmission of X-rays through matter may be readily explained in terms of a few simple laws expressed with reference to these spectra.

[I wish to express my indebtedness to Mr. G. H. Martyn for his assistance in some of these experiments.—C. G. B.]

*XL. The Intensity of the Ultra-Violet Light emitted by an Electrical Discharge at Low Pressures. By E. W. B. GILL, M.A., B.Sc., Fellow of Merton College, Oxford\*.*

THE phenomena accompanying the discharge of electricity through gases at low pressures have been examined in great detail by many observers, and accurate measurements have been made of the distribution of electric force along the discharge, the number of ions at various points, the temperature and other properties.

The experiments here described are a set of measurements of a different nature relating to the distribution of intensity of the light emitted, or more strictly of the intensity of a certain portion of the spectrum of the light emitted from various parts of the discharge. The results obtained, though not throwing much light upon the actual mechanism of the discharge, are of some interest as showing a systematic variation with change of pressure of rather a curious kind.

When ultra-violet light falls upon a metal plate, zinc being usually used, negative ions are set free at its surface; and Griffiths has shown that, other things being equal, the number of ions set free is nearly proportional to the intensity of the light.

An estimate of the number of ions set free by the light coming from different portions of the tube will therefore give at once the relative intensities. A previous research† has shown that the rays chiefly instrumental in setting free the ions vary from about  $250\ \mu\mu$  to  $180\ \mu\mu$ , and it must be understood that the results of these experiments refer to the intensity of this particular range of wave-lengths.

#### *Description of Apparatus.*

The discharge-tube was constructed of quartz, and was joined to a large glass reservoir containing mercury in its

\* Communicated by Prof. J. S. Townsend.

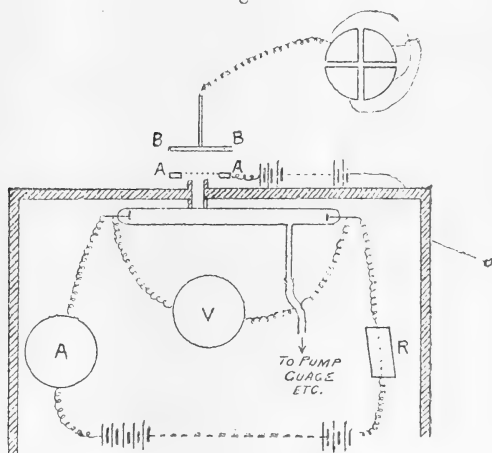
† Phil. Mag. Feb. 1910, p. 290.

lower part. Any desired pressure could be obtained by exhausting the apparatus with a mercury pump and then adjusting the level of the mercury in the reservoir. The pressure was read on a McLeod gauge. A drying-tube was also inserted.

The electrodes were circular disks of aluminium about 1.5 cm. in diameter and distant apart 7.5 cm.; the connecting wires being fused through the quartz and the seal covered with mercury to prevent any air-leak. The electrodes were first of all subjected to a discharge for a considerable time to drive off all traces of hydrogen and other occluded gases.

The apparatus is depicted diagrammatically in fig. 1. To

Fig. 1.



get a steady discharge a very large number of small storage-cells were connected in series and joined through an ammeter to the terminals of the tube, a large resistance  $R$  being in the circuit. The current was very small (about 4 milliamperes), the storage-cells being able to give this without running down, and the current could be conveniently measured on the sensitive part of a Nalder combined ammeter and voltmeter.

The drop of potential down the tube was measured by a Kelvin electrostatic voltmeter  $V$ .

The tube was contained in a lead box (shown shaded) having a vertical slit 1 cm. wide cut in the side; and the tube was mounted in such a way that any portion of its length could be placed in front of this slit.

The light emerging from the slit passed through a wire gauze AA and fell upon the zinc plate BB connected to an electrometer; the distance between the plate and gauze being about 1 cm. AA was charged up to +40 volts by connexion to a battery of small cells, and BB was initially at zero potential and insulated. The plate and gauze were carried upon ebonite supports.

*Method of conducting an experiment.*

In any set of observations the discharge was always passed for a fixed time, usually 20 seconds. The first centimetre of the discharge beginning from either electrode was placed opposite the slit and light from it fell upon the zinc plate, a certain number of negative ions  $n_1$  were set free, were attracted to the gauze AA, and in consequence the electrometer showed a deflexion  $\delta_1$ . After earthing and again insulating the electrometer a deflexion  $\delta_2$  was obtained, due to  $n_2$  ions being set free by the light from the second centimetre of the discharge, nothing except the tube having been moved. Then  $\frac{\delta_1}{\delta_2} = \frac{n_1}{n_2}$  = the ratio of the intensities of the UV light from these two portions of the tube.

As explained above, care was taken to keep the pressure of the air inside the tube constant, and owing to the small leak no other gas except air was used in the tube. [It is possible that small changes of pressure that occurred were due to chemical action.]

The deflexions of the electrometer were always small, which accounts for the choice of such a comparatively large slit (1 cm. broad) in order to get a measurable ratio not too much affected by errors of experiment. The relative intensities of each cm. of tube were thus obtained, and in a few cases of interest several cms. overlapping were taken as well.

It is obvious that the intensity depends upon three variables, the pressure  $p$ , the current  $c$ , and the potential difference between the electrodes  $V$ ; these variables not being independent but being connected by one relation. Looking upon  $p$  and  $c$  as independent variables, a complete research would determine the distribution of intensity for all values of  $p$  and  $c$ , but the value of the results scarcely warrants so laborious an undertaking, and all the experiments were conducted for a constant current,  $p$  being taken as the only independent variable. A few preliminary experiments, however, showed that for the higher pressures (1 to 2 mm. of mercury) the intensity was approximately proportional to

the current, but it is doubtful if this is so for the lower pressures. The current in all the following results was always 4 milliamperes.

This current was obtained partly by varying the number of cells in series with the discharge-tube, and partly by altering the resistance  $R$ . At the higher pressures the discharge usually required to be started by connecting one only of the terminals to one of the poles of an induction-coil for an instant; but at the lower pressures the discharge practically always started itself. The lead box being connected to earth was useful in shielding the detecting apparatus from disturbances due to the coil and other sources; the coil (not shown) being in the box.

The distribution of intensity was obtained as the mean of several sets of readings for several different pressures, and the whole set were then connected by fixing the tube at a position which gave a large intensity in most of these cases, reproducing these different pressures, and getting the corresponding deflexions. The intensities could thus be all expressed in terms of some arbitrary unit.

#### *Plotting the Results.*

The distance between the electrodes being  $7\frac{1}{2}$  cm., a distance of  $7\frac{1}{2}$  units was marked off along the axis of  $x$ , the anode being at the origin and the cathode at the point 7.5. The intensity of the light from the first cm. of tube beginning at the anode was taken as ordinates at pt  $x=.5$ , from the second cm. at  $x=1.5$  and so on, and from the last cm. which overlapped the previous one at  $x=7$ . By this means the curves figs 2-6 were obtained (pp. 416-418).

The current as already stated being always 4 milliamperes, the pressure being given in millimetres of mercury, and the potential difference  $V$  between the electrodes when current was passing in volts.

#### *Discussion of Results.*

The anode is in all the figures at the origin and the cathode to the right, and it will be seen that for all the pressures considered the emission of ultra-violet light from the half centimetre beginning at the cathode is practically negligible. The very large cathode fall of potential (about 340 volts) does not extend beyond this space, and the results therefore confirm the theory that practically all the energy in this space is devoted to forming fresh ions by collisions, and very little of the energy is available for emitting radiations.

The most interesting result of the experiments is, however, the systematic variation with the pressure. In fig. 2 starting

Fig. 2.

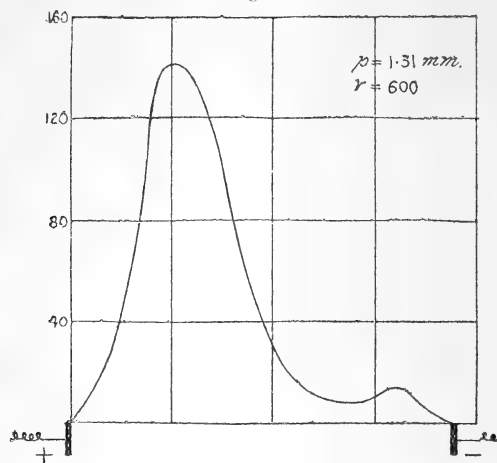
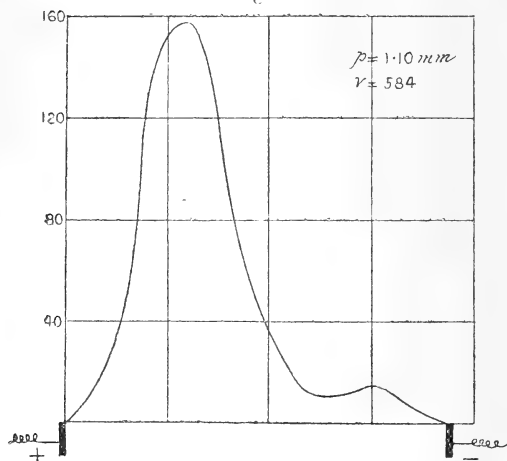


Fig. 3.



with the higher pressures the greater part of the light comes from the left end, that is the end nearer the anode, the amount from the centre being small; the same is true for the slightly lower pressure in fig. 3, the fact that the maximum is a little higher than in fig. 2 is probably due to errors of experiment. In fig. 4, although the general features are still the same, the right-hand maximum is beginning to become more prominent.



Somewhere between figs. 4 and 5 the minimum sparking potential for the particular tube occurs, the minimum potential

Fig. 4.

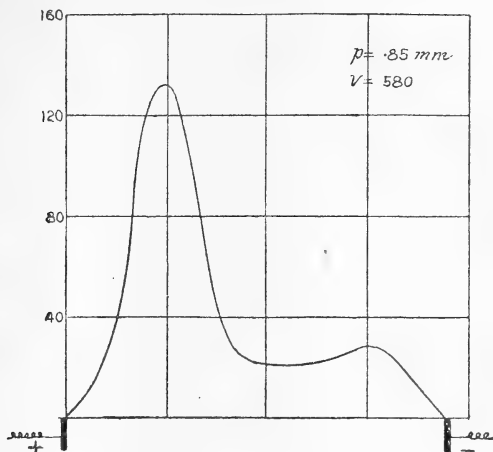
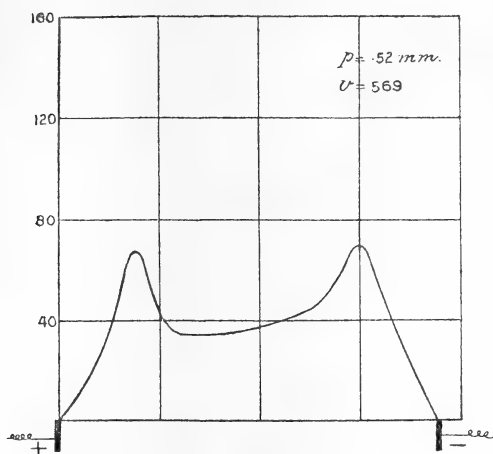


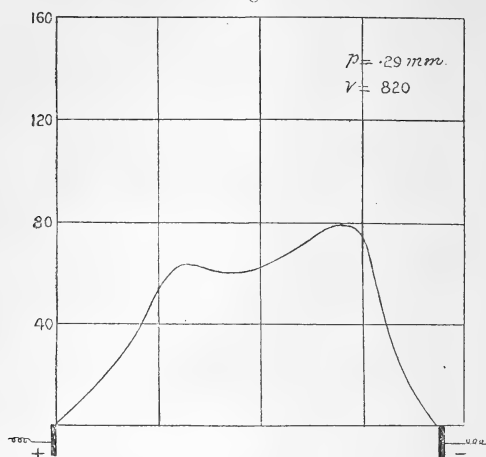
Fig. 5.



being roughly estimated at 560 volts, and after passing this point a very decided difference is apparent. In fig. 5 not only have the two maxima become about equal but the light from the centre of the tube has also become large, while with

the lowest pressure investigated .29 mm. of mercury, fig. 6, the left-hand maximum has almost disappeared, the centre

Fig. 6.



light having become equally important, and the highest maximum is then on the right. In these last cases the discharge lit up the whole tube and discharges occurred round the back of the electrodes.

The effects were all due to UV light, no trace of Röntgen rays was found nor of Entladungstrahlen, for no deflexion could ever be obtained if the zinc plate was charged positively, or if when negatively charged a very thin sheet of aluminium was interposed to cut off the light.

The tube was unfortunately too short to show much positive column, and I doubt if more than 2 or 3 cm. of column were present in any experiment. It would have been interesting to have continued the measurements to still lower pressures, but the potential difference required to drive the discharge soon gets so enormous that there were not sufficient cells available to proceed further.

The results, however, without assuming any theory as to the actual mechanism by which the short waves of light are emitted, are certainly sufficient to show that, after the pressure corresponding to the minimum sparking potential for two fixed electrodes has been passed, the character of the discharge is radically changed.

This research was suggested by and conducted in the laboratory of Professor Townsend, to whom my thanks are due for very much encouragement and assistance.

XLI. *The Disintegration Products of Uranium.*

By G. N. ANTONOFF\*.

IT is now generally accepted that uranium is the primary substance from which ionium and radium with its series of products are derived. In old minerals, all  $\alpha$  ray products in radioactive equilibrium with uranium emit an equal number of  $\alpha$  particles per second except uranium itself, which emits twice as many. Consequently either two  $\alpha$  particles are emitted at the disintegration of each atom, or the uranium is in equilibrium with an unseparated  $\alpha$  ray product.

Actinium and its products also occur in minerals in constant ratio to uranium, but their total activity is much weaker than that of uranium. Boltwood† has shown that the total activity of actinium together with its products is about 28 per cent. of uranium. In explanation of this, Rutherford and others have suggested that actinium is a lateral branch arising at one stage of the uranium-radium series.

Thorium, although it is almost always present in uranium minerals, is supposed to be an independent radioactive element, because its ratio to uranium in minerals varies within wide limits.

The investigation of radioactive minerals from the point of view of the disintegration theory has made it clear that ionium and radium &c. are disintegration products of uranium. Also the growth of radium in uranium salts has been directly observed‡. On the other hand, it is known that UrX is a direct product of uranium, but at present no definite evidence of the transformation product of the former has been obtained. It has been pointed out by Danne§ that UrX separated from a large quantity of uranium leaves a constant  $\alpha$  ray activity after complete disintegration. It is not known whether this  $\alpha$  ray product has actually grown from UrX, or has been separated from uranium, which generally contains very many radioactive impurities. Soddy||, however, came to the conclusion that UrX completely loses its activity with time. Several attempts have also been made to observe the growth of actinium in uranium. The experiments carried out by Soddy¶ showed that actinium could be detected in some uranium preparations, but no proofs were given that the original preparations were free from actinium.

\* Communicated by Prof. E. Rutherford, F.R.S.

† Boltwood, Amer. Journ. Sci. xxv. p. 269 (1908).

‡ Soddy, Nat. lxxx. p. 308 (1909): *Phys. Z.* x. p. 396 (1909).

§ Danne, *Le Radium*, vi. p. 42 (1909).

|| Soddy, Phil. Mag. xx. p. 342 (1910).

¶ Soddy, *Loc. cit.*

Some irregularities in the behaviour of UrX have been noted by several investigators. Variations of the  $\beta$  ray activity in uranium were observed by Meyer and von Schweidler\* in 1904. The question was examined later by Godlewski †, who ascribed the abnormal behaviour to the diffusion of UrX. Meyer and von Schweidler also found a rapid decay in some preparations, indicating the presence of a product with a period of about 2 days. Becquerel ‡ separated from uranium by charcoal some radioactive substance whose activity grew in 8 days to one and a half times its original value. Later Levin § repeated Becquerel's experiment, but could not separate anything but UrX.

Soddy || found that during the first ten days of decay some preparations of UrX decay faster than the normal rate.

In all these investigations no evidence of the purity of the uranium preparations has been given. The present research was undertaken with preparations of uranium from which all known radioactive impurities had been separated.

An account of the literature about uranium and its products may be found in a review by St. Meyer (see *Jahr. d. Rad.* vi. 1909, p. 381).

### *Experiments with Uranium X.*

As commercial uranium nitrate, even extra pure, generally contains very many radioactive impurities, several methods of purification were employed with the view of separating radium, actinium, and thorium with their series of products. These methods will be fully described later in the paper, but it may be mentioned here that special tests of the uranium preparations have afforded a definite proof that all radioactive impurities have been removed. The UrX was separated by two methods. The first consists in precipitating barium in the uranium solution as  $\text{BaSO}_4$ , and the second in adding an iron salt to the uranium solution and precipitating it by boiling. These methods will be hereafter called the *barium* method and the *ferrie* method respectively.

It is known that UrX emits soft rays with an absorption coefficient in aluminium  $\mu = 500 \text{ (cm.)}^{-1}$ , and hard rays with  $\mu = 14 \text{ (cm.)}^{-1}$ . The activities of the UrX preparations were measured first when uncovered, and afterwards through 0.01 cm. of aluminium. The first measurement gave the

\* Meyer and v. Schweidler, *Wien. Sitzber.* cxiii. p. 1057 (1904).

† Godlewski, *Phil. Mag.* x. p. 45 (1905).

‡ Becquerel, *C. R.* cxli. p. 87 (1905).

§ Levin, *Phys. Z.* vii. p. 692 (1906).

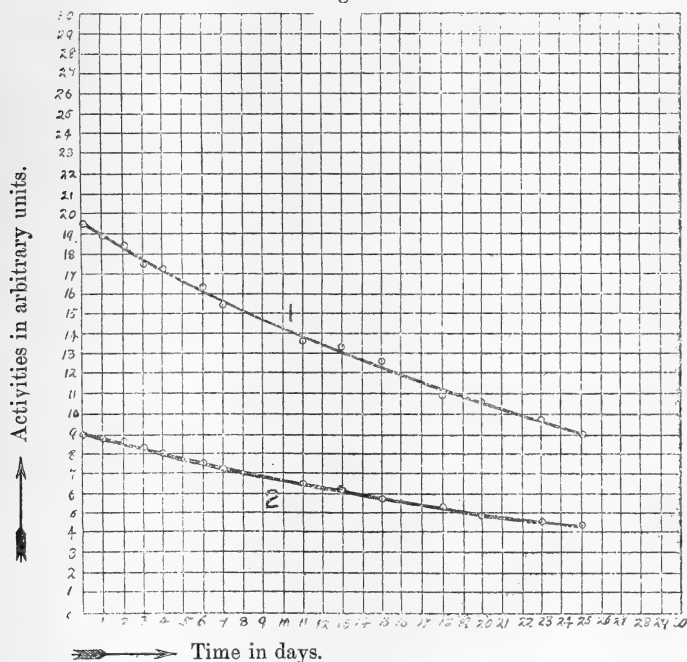
|| Soddy, *Phil. Mag.* xix. p. 847 (1910).

total activity, and the second the activity due to the hard rays.

UrX separated from uranium by the barium method gives for both types of rays exponential decay curves with practically identical periods. Also the absorption curves of such preparations taken at different intervals after separation are always of the same shape, indicating that the UrX contains no other active product.

When UrX is separated by the ferric method, a *rapid initial drop* in the decay curve is always observed, if the preparation is *uncovered*. The activity of the UrX thus prepared, when measured through 0.01 cm. or more of aluminium, decays exponentially with the same period as the preparations obtained by the barium method. The absorption curves of the ferric preparations show the presence of a much larger quantity of soft  $\beta$  rays than is found in the barium preparations.

Fig. 1.

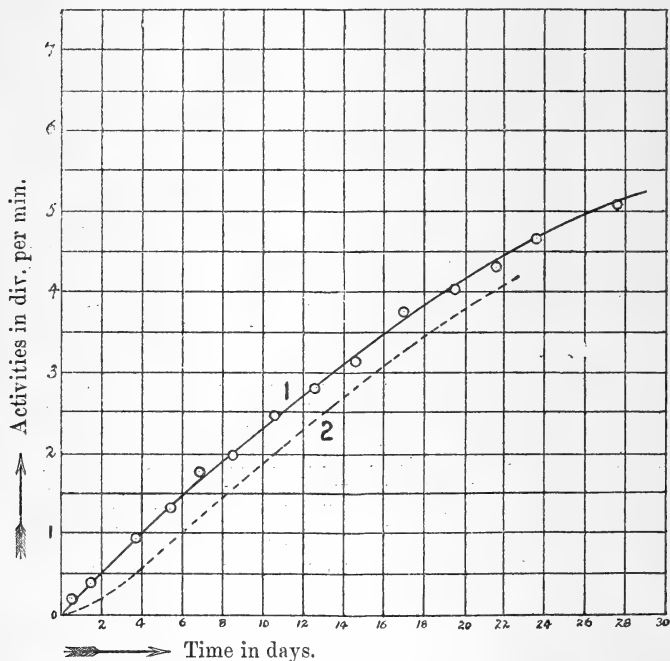


The experimental results for the barium preparations are given in fig. 1, and plotted as curves 1 and 2. Curve 1 gives the activities of an uncovered preparation, and curve 2 those through 0.01 cm. of aluminium.

The curve for hard rays gives a half period of 23.5 days. The curve for the uncovered preparation seems to give a slightly lower period of about 23.0 days, but the difference is within the limits of experimental error.

To obtain the recovery curve of uranium, the  $\text{UrX}$  was completely separated from uranium by boiling the solution of uranium nitrate with a large quantity of ferric oxide. The ferric oxide was filtered off and the above process repeated several times. The uranium nitrate was converted into oxide, which was spread on a tray and placed under a  $\beta$  ray electroscope. Its activity was measured for several months. The initial value soon after the separation was found to be 0.05 div. per minute. The constant maximum value after several months was found to be 9.2 divs. per minute. The half value was reached after about 23.5 days,

Fig. 2.



corresponding to the half period found from the decay of  $\text{UrX}$ . Curve 1 in fig. 2 shows on a large scale the initial part of the theoretical curve calculated from the equation  $I/I_0 = 1 - e^{-\lambda t}$ , where  $I_0$  is the maximum activity and  $I$  is the activity at any time  $t$ , taking for  $\lambda$  the value corresponding

to a half period of 23.5 days. The points marked on the curve show the values obtained experimentally. It is seen that they agree with the theoretical curve within the limits of experimental error. There is thus no evidence of any intermediate change between uranium and  $\text{UrX}^*$ .

### *Experimental Method.*

Before discussing the results obtained with ferric preparations, it is necessary to describe briefly the method employed to detect the soft radiations when mixed with the radiation of  $\text{UrX}$ . As  $\text{UrX}$  separated from pure uranium by the ferric method is accompanied by some soft radiation, a special experimental arrangement was adopted to measure all soft and hard rays under the same conditions. A  $\beta$  ray electroscope with its opening covered with thin aluminium sheet of 0.00025 cm. thickness was employed. The radioactive preparation was clamped to the bottom of the electroscope so as to be directly under the opening, and always in the same position. The sheets of absorbing material were placed between the opening and the radioactive preparation, and were thus compressed by the clamp. Special care was taken to avoid any displacement of the radioactive preparation when large thicknesses of foil were used. In this way it was possible to obtain practically the full effect in the electroscope of the hard and soft  $\beta$  rays. The  $\alpha$  ray effect is, however, diminished more than that due to the  $\beta$  rays, because they have to pass through about 0.8 cm. of air before reaching the aluminium foil, whose thickness is equivalent to 0.5 cm. of air, or in other words, the loss of  $\alpha$  ray activity is that due to a shortening of the range by 1.3 cm. of air. This experimental arrangement is convenient for taking absorption curves because the aluminium foil prevents air currents in the electroscope. In some cases, however, when a stronger effect from the  $\alpha$  rays was desired, the measurements were taken in an identical electroscope without an aluminium foil. In this case there was no absorption of the radiation, and the ionization produced corresponds to the whole path of the  $\alpha$  rays. The absorption curves for the preparations of pure  $\text{UrX}$  show that if the film is very thin, the ratio of the total activity to that of the preparation measured through a standard sheet of 0.01 cm. of aluminium, which allows only the hard rays of  $\text{UrX}$  to pass, is invariably 2.15 under the experimental conditions. If  $\text{UrX}$  is accompanied by some additional soft rays this ratio is much higher,

\* The meaning of the dotted curve 2 will be explained later.

and in some cases the activity does not decay exponentially if measured without absorbing screens. However, the radiation passing through 0.01 cm. of aluminium decays normally with the same period as the pure barium preparations. Therefore if the activity of the preparation is measured through 0.01 cm. of aluminium, and the value obtained multiplied by 2.15, the total activity at any time due to UrX alone can be calculated. The UrX activity is then subtracted from the total activity to obtain the activity of the product mixed with it.

*The Product.—Its Decay and Absorption.*

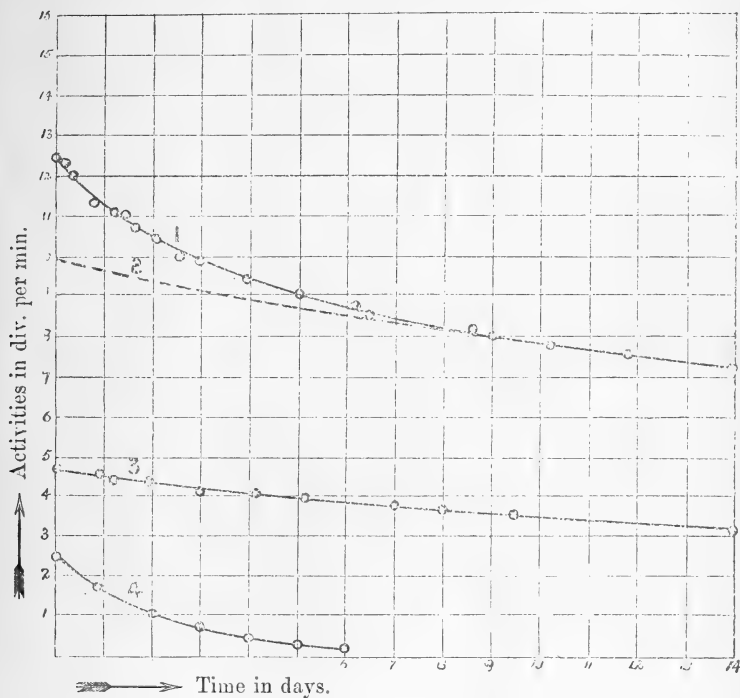
The ferric preparations were examined by the method already described, and several curves were obtained showing that a soft ray product which decays in a few days is always present in small quantity. Several attempts were made to separate a large quantity of this product from uranium, but in all cases its activity is small compared with that of the UrX with which it is separated. Owing to the very similar chemical properties of UrX and the new product, it was not found possible to isolate the latter, for it was always accompanied with UrX\*. When UrX and the product are separated from uranium in equilibrium by the ferric method, a preparation is obtained containing so much UrX that it is sometimes difficult to measure its activity with the electroscope. Further separations bring down less and less of UrX and the product. The separation is then repeated after allowing it to stand for a few days. The new product is then separated with comparatively little UrX. To determine the absorption of the radiation it is necessary to prepare very thin films. For this purpose the method of separation was sometimes modified. The uranium was dissolved in a half normal solution of ammonium carbonate, a trace of ferric salt added, and the solution boiled and filtered. The iron precipitate was washed with ammonium carbonate solution to remove the traces of uranium, and the filter-paper was then burnt; the ashes in a very thin layer were placed on a tray. In this way, although it was necessary to work with large volumes, it was easy to make the separation with only minute traces of iron. These preparations were examined by the electroscope already described. The decay curves are given in fig. 3.

\* Information on the chemical properties of UrX may be found in the paper by Lloyd, J. of Phys. Chem. xxiv. p. 509 (1910). See also Keetman, *Jahr. d. Rad.* vi. p. 265 (1909).



Curve 1 is the decay curve of the uncovered preparation, and curve 3 the decay curve through 0.01 cm. of aluminium.

Fig. 3.



If the activities in curve 3 are multiplied by 2.15, curve 2 representing the total activities of UrX is obtained. Curve 4, which is the decay curve of the product, was obtained by taking the difference between curves 1 and 2. It should be noted that curve 2 coincides with curve 1 about ten days after separation of the uranium X, indicating that no other product except UrX then remains.

The period of the new product deduced from the curve is 1.5 days. A number of other curves obtained in a similar manner gave about the same period of decay. It is proposed to call the new product uranium Y (UrY).

It is now necessary to consider the types of radiation emitted by this new product. Special experiments were made to test whether any  $\alpha$  rays were present. It is

known that UrX emits only  $\beta$  rays, and no appreciable quantity of uranium was present in the film. The new product, UrY, and UrX, were separated with as little material as possible, then spread on a small area, and placed immediately under a zinc sulphide screen. After the eye had been thoroughly rested in a dark room, the scintillations were counted by a low-power microscope. Immediately after separation, 2-3 scintillations per minute were observed. The average number could be measured with sufficient accuracy by taking a large number of readings. The counting was continued during three days, and the average number of scintillations were found to diminish. The period could not be determined with accuracy; but the results indicated that the  $\alpha$  rays were emitted by a product whose half period of decay was about 1.5 days. Finally, the number of scintillations became too small in number to be counted.

These experiments indicate that UrY emits some  $\alpha$  rays; but at the same time it should be pointed out that the number of  $\alpha$  particles observed is small compared with that to be expected from the  $\beta$  ray activity of the product. Experiments of this character, where only one or two scintillations appear per minute in the microscope, are very difficult, but every precaution was taken to avoid error.

Further evidence in support of the view that UrY emits  $\alpha$  particles can be obtained from an examination of the initial part of the absorption curve.

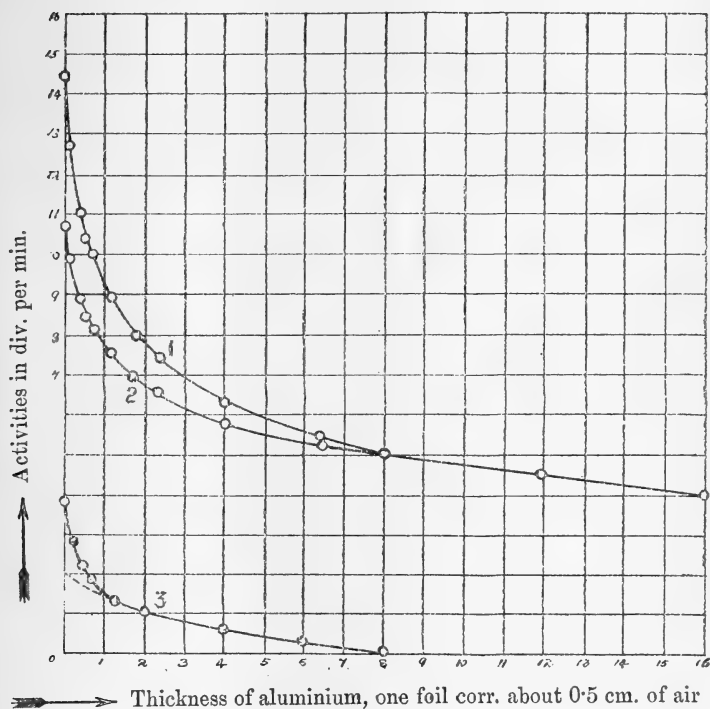
A preparation, in which the activity of the product was about 30 per cent. of that of the UrX mixed with it, was examined and its absorption curve was taken immediately after the separation. To determine the absorption of the product it is necessary to subtract the absorption of pure UrX. This can be accomplished either by taking a barium preparation or a ferric preparation after the short-lived product has completely decayed. The absorption curves are shown in fig. 4 (curves 1 and 3).

Curve 1 is the absorption curve of UrX and the product and curve 2 is that of pure UrX. The two curves were reduced to the same scale by equating the values of the activities through 0.01 cm. of aluminium. It is seen that for hard rays the absorption curves are identical.

Curve 4 was obtained by taking the difference between 1 and 2, and it represents the absorption curve of the product. This curve shows a rapid initial drop, which corresponds to the  $\alpha$  ray effect diminished by 1.3 cm. of air. The remainder

of the curve is practically an exponential curve with  $\mu$  about  $300 \text{ (cm.)}^{-1}$  for aluminium.

Fig. 4.

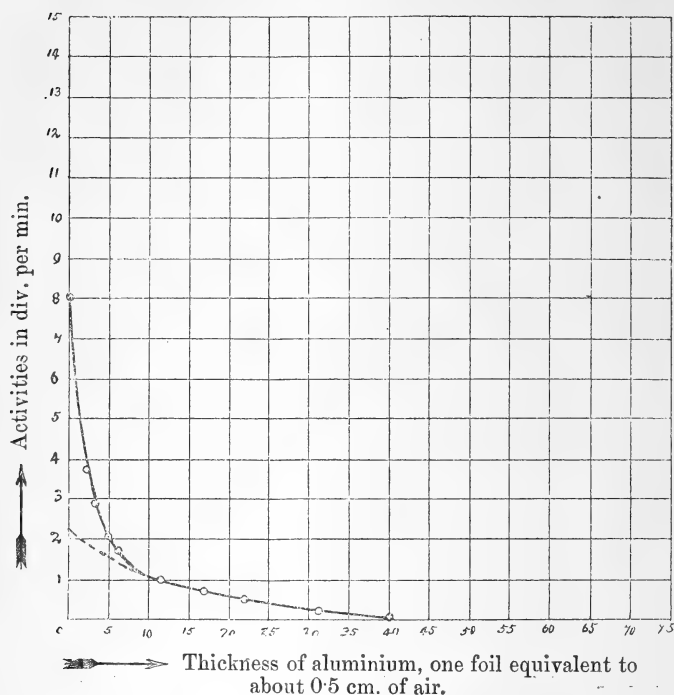


In the above experiments the electroscope was covered with  $0.00025 \text{ cm.}$  of aluminium; but if the electroscope was used without an aluminium leaf, the effect due to the product is a little more than doubled (see fig. 5, p. 428).

The  $\beta$  radiation is about 25 per cent. of the total, and the absorption coefficient of the  $\alpha$  rays in aluminium calculated in the ordinary way is about  $2500 \text{ (cm.)}^{-1}$ , and is about that to be expected for  $\alpha$  rays of average range. "his  $\alpha$  ray effect cannot be attributed to a small quantity of uranium in the film, for it is seen that the rapid drop in the absorption curve disappears in a few days. The preparations were examined after about two months, and it was found that the activity due to traces of uranium could be only about  $0.1 \text{ div. per}$

minute. (In figs. 3 and 4 the activities are expressed in terms of the number of divisions per minute actually observed in the electroscope.)

Fig. 5.

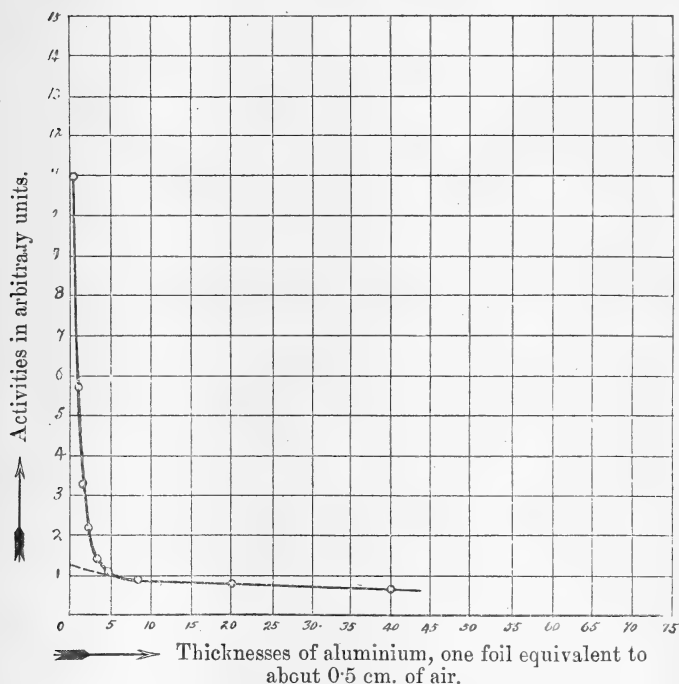


### *The Position of the New Product.*

Since UrY is always present in purified uranium, it follows that it must be derived in some way from that substance. From a given quantity of uranium, only a small amount of UrY could be separated at a time. It was calculated that the electric effect due to UrY, under the experimental conditions, was only about  $1/60,000$  of the total  $\alpha$  ray effect due to the amount of uranium from which it was separated. The first separations by the ferric method remove most of the product, and when the successive separations are made at short intervals, the amount separated becomes much smaller. It consequently follows that either this product is present in very small quantities or the method of separation is almost ineffective. In the latter case it is natural to suppose that

UrY is the second  $\alpha$  ray product in uranium. However, the following consideration shows that such is not the case. If UrY is the second product in equilibrium with uranium, its  $\alpha$  ray activity should be equal to about one half the total activity of uranium. Since the product shows a strong  $\beta$  ray effect compared with the  $\alpha$  ray effect, the absorption curve of uranium should indicate the presence of a large proportion of the soft rays characteristic of the product. However, the absorption curve (see fig. 6) of uranium in a

Fig. 6.



thin layer shows that besides  $\alpha$  rays only the rays of UrX can be detected. Consequently it does not appear probable that UrY is the second product in uranium.

In considering the possible position of this product in the uranium series, several factors have to be taken into consideration. The evidence indicates that the new product is not transformed into UrX, for we have seen that the  $\beta$  ray rise curve of uranium, from which UrX and UrY were separated by the ferric method, is quite normal in its initial

stages. If  $\text{UrY}$  is intermediate between uranium and  $\text{UrX}$ , the rise curve to be expected is shown by the dotted curve in fig. 2. There is no evidence that  $\text{UrY}$  is in this sense an intermediate product between uranium and  $\text{UrX}$ . At the same time, it should be pointed out that it is difficult to draw such a conclusion with certainty, for it is based on the assumption that all of  $\text{UrY}$  is separated with  $\text{UrX}$ .

The principal difficulty encountered is that there is no direct method of showing that  $\text{UrY}$  is completely separated. In the case of  $\text{UrX}$ , the proof of complete separation is quite simple on account of the quantity of  $\text{UrX}$ , and the penetrating power of its rays, while the comparison of the  $\beta$  ray activity of uranium before and after separation of  $\text{UrX}$  is quite definite. There is, however, some indirect evidence that  $\text{UrY}$ , under certain conditions, is also completely separated, for with small quantities of iron used in successive precipitations both  $\text{UrX}$  and  $\text{UrY}$  were obtained in diminishing quantities. Large quantities of iron are favourable to a complete separation, but on account of the soft radiation of  $\text{UrY}$  small quantities of iron had to be used to obtain thin films. With large quantities of iron, the  $\text{UrX}$  can be separated completely after a few precipitations, as was shown on page 422. It seems very probable that, under such conditions,  $\text{UrY}$  must be also precipitated more or less completely.

When large quantities of iron are used in the precipitation  $\text{UrX}$  and  $\text{UrY}$  are separated with a thick layer of iron. In consequence of the absorption of the  $\beta$  rays in this layer it is difficult to draw any definite conclusions from such an experiment in regard to the relative amount of radiation due to the two products. On the other hand, the initial part of the recovery curve of  $\text{UrX}$  in uranium, treated with a large quantity of iron, should show some indication of the presence of  $\text{UrY}$  if it is an intermediate product; but, as we have seen, the recovery curve is quite normal.

It may be mentioned here that the  $\alpha$  ray activity of a film of uranium of known weight before and after treatment with a large quantity of iron was determined; but no appreciable change of  $\alpha$  ray activity was observed.

In addition  $\text{UrY}$  does not seem to be a direct product (immediate or otherwise) of  $\text{UrX}$ , for in such a case one would expect larger quantities of it in old preparations than in those freshly prepared. On the contrary, experiments showed that the amount separated from uranium several years old is of the same order as that separated after a few days from freshly purified uranium.

It is difficult at the present time to draw any very definite conclusion of the connexion of  $\text{UrY}$  with the uranium series, but the general results indicate strongly that  $\text{UrY}$  is not a product in the main series, but is a *branch product of uranium*.

### *Purification of Uranium.*

100 gr. of uranium nitrate were taken and  $\text{BaCl}_2$  was precipitated in it several times as  $\text{BaSO}_4$ . Subsequently the uranium nitrate solution was evaporated to dryness and kept at  $110^\circ \text{C}$ . It was then extracted with dry ether and crystallized three times as nitrate. Some ferric oxide was added to the above uranium nitrate solution and separated after boiling. It was found by measuring the decay curve that a considerable amount of soft rays not belonging to  $\text{UrX}$  was present. From the above curve the decay curve of  $\text{UrX}$  was subtracted. The resultant decay curve was of the same nature as the one obtained when ferric oxide was added and separated from an actinium solution. It was, therefore, very probable that actinium was not separated by the ordinary extraction with ether.

The following method was afterwards employed. A kilogram of uranium nitrate was taken and  $\text{BaSO}_4$  was precipitated in it three times. Since actinium and lanthanum are precipitated together, 10 gr. of lanthanum nitrate were added to the uranium solution and precipitated by adding an excess of a hot solution of ammonium oxalate. After 24 hours the precipitate of lanthanum oxalate was filtered off, and the uranium twice crystallized as double ammonium uranium oxalate. Then the uranium was again converted into nitrate and 10 gr. of lanthanum nitrate were again added. The solution was evaporated to dryness, kept at  $110^\circ \text{C}$ ., and the uranium was extracted with dry ether and crystallized twice as nitrate. The lanthanum was found to be very active. It was converted into nitrate and boiled with an excess of  $\text{Na}_2\text{S}_2\text{O}_3$ . The precipitated sulphur entrained  $\text{UrX}$ , and after ignition a strong preparation of  $\text{UrX}$ , without a visible amount of weighable substance, was left. After six months a part of the above uranium, converted into oxide, was placed on a tray  $18 \times 18 \text{ cm.}$ , and a plate of the same size connected with the negative pole of a battery placed above it, for 24 hours. No traces of actinium or thorium active deposit could be detected on the plate.

Another kilogram of uranium nitrate was treated in a different way. To it was added some thorium from which mesothorium had been separated, and afterwards an excess of a hot solution of oxalic acid. After a few days the

scarcely soluble uranium oxalate was separated from the mother liquor by suction, and dissolved in a large quantity of hot water. It was then filtered, evaporated to dryness, and converted into the nitrate. This uranium nitrate might possibly have contained traces of thorium, because the thorium oxalate might have gone through the filter-paper. Therefore some inactive rare earth was added and separated as above.

After these separations,  $\text{BaSO}_4$  was precipitated three times in the uranium solution with the object of separating radium and mesothorium if present. Then a mixture of lead and bismuth was added and precipitated with  $\text{H}_2\text{S}$  to separate polonium if present, and finally uranium was twice crystallized as nitrate.

The first method was employed for the separation of actinium, and is convenient because of the considerable solubility of uranium oxalate in ammonium oxalate. The second method, although very difficult because of the small solubility of uranium oxalate in water, was employed to separate with thorium both actinium and ionium.

Both preparations of uranium showed only the growth of  $\text{UrX}$  and the product with the period 1.5 days. All these precautions were necessary since the method used for the separation of  $\text{UrX}$  separates in addition actinium and its products, thorium X, mesothorium and polonium.

#### *Summary.*

- (a) It has been shown that a product called  $\text{UrY}$  with a period 1.5 days is always present in small quantities in uranium. It emits soft  $\beta$  rays with an absorption coefficient  $\mu = 300 \text{ (cm.)}^{-1}$  and probably also some  $\alpha$  rays.
- (b) In its chemical nature the product is very similar to  $\text{UrX}$ , and it has not been found possible to separate it chemically from the latter.
- (c) The experimental results described in this paper indicate that  $\text{UrY}$  is a lateral disintegration product of uranium and is produced in small quantity compared with  $\text{UrX}$ .

In conclusion, I wish to express my best thanks to Professor Rutherford for placing the necessary facilities at my disposal, and for the interest he has taken in the work.

University of Manchester,  
June 1911.



XLII. *Increased Accuracy in the Use of Bifilar Suspensions.*  
 By A. NORMAN SHAW, M.Sc., R. O. King Research Fellow,  
 and Lecturer in Physics, McGill University, Montreal\*.

IN the case of single suspensions it is well known that many materials exhibit complicated movements after the wire or fibre has been twisted first in one direction and then in the other for a considerable number of times. As it is often necessary in practice to employ suspensions whose direct elastic properties are constant, the choice of a material which shall also have a minimum elastic after-effect becomes a difficult matter. A thorough search for a suitable suspension was recently made by K. E. Guethe, at the Bureau of Standards in Washington, in connexion with his determination of the electromotive force of standard cells, but he states that the attempt was only "partially successful"†. A large number of investigators have examined this phenomenon of elastic after-effect, and its behaviour has often been pointed out as being analogous to that of electric absorption in condensers‡. The theory of the subject was, indeed, developed first for this "elastische Nachwirkung" by Weber, Kohlrausch, Meyer, Boltzmann, Natanson, and others, and then applied to the analogous case of absorption§. Schweidler gives a very complete list of papers on this subject in the *Ann. der Physik*, vol. xxiv. 1907, on page 711.

In the choice of bifilar suspensions, it is desirable that the wire should have, in addition to a minimum after-effect, an especial constancy of length under strain, and an absence of appreciable flexural rigidity at the extremities of the suspensions. Although the controlling couple in the bifilar suspension is affected by the elastic after-effect to a much less degree for a given substance than the single suspension, yet the satisfying of all the requirements has rendered it a difficult matter to obtain a suitable material. The constancy of the main factor in the controlling couple suggests the possible attainment of great accuracy in the use of bifilar

\* Communicated by Prof. H. T. Barnes, F.R.S.

† Guethe, *Bull. Bur. of Stan.* vol. ii. 1906, p. 33; McCollom, *Bull. Bur. Stan.* vol. vi. 1910, p. 503.

‡ Hopkinson, *Phil. Trans.* vol. clxvi. 1876, p. 489, and *Proc. Roy. Soc.* vol. xxviii. 1878, p. 148; Trouton and Russ, *Phil. Mag.* vol. xiii. 1907, p. 578.

§ Weber and Kohlrausch, *Pogg. Annal.* Bd. liv. pp. 119 & 128; Kohlrausch, *Zeitschr. Gesammt. Naturwiss.* vol. xiii. 1876, p. 368; Meyer, *Annal. Phys. Chem.* vol. iv. 1878, p. 249; Boltzmann, *Sitzungsberichte der k. Akad. der Wiss. zu Wien*, Bd. xl. 1874, p. 275; Natanson, *Bull. de l'Acad. des Sciences de Cracov*, Oct. 1902, p. 512.

suspensions, but these difficulties have caused it to fall somewhat into disuse. It is the purpose of this paper to suggest a method for treating the bifilar suspension in order that it may be more successfully employed for observations involving very refined measurements.

The investigation has been performed in connexion with a research on the absolute measurement of the electromotive force of the Weston standard cell by means of the Weber electro-dynamometer. This instrument was purchased by McGill University as a part of the general equipment of the Macdonald Physics Building about 1893. It was carefully made by Nalder, and was an exact copy of the dynamometer constructed by the Electrical Committee of the British Association, and described by Maxwell\*. The instrument was set up by Mr. R. O. King in 1895, under the direction of Prof. Callendar. The work by Mr. King has been fully described by Callendar†, who made some important changes in its windings. Preliminary observations were obtained by Mr. King for the electromotive force of the old Board of Trade form of crystal Clark cell, and it was intended that more accurate work should be obtained later. This work was not, however, carried out, and the dynamometer remained in disuse for over ten years. It was suggested by Prof. Barnes that the writer should complete this investigation, and through the generosity of Mr. King, a Fellowship was provided, which enabled him to devote a year almost without interruption to the work. It was found, during the series of observations on the deflexion measurements, that there was a serious difficulty due to a small elastic after-effect, which rendered this part of the work less accurate than the other. In order to study this more carefully, the writer devoted a considerable amount of time to determining the effect of repeated deflexions on the true reading of the instrument. It was found possible to systematize the results in a satisfactory manner, and work out mathematically the equations for determining the correction to be applied in any particular case. In many ways this was an unusually good opportunity to test the constancy of bifilars. The suspended coil had been hanging for over ten years, and it was thought that the wires would be as permanent in their behaviour as any of the kind could be expected to be. They were made of hard drawn copper, diameter 0.0450 cm., length 80 cm., and were rigidly clamped 3.1 cm. apart.

This suspension fulfils remarkably well all the requirements

\* 'Electricity and Magnetism,' (3rd ed.) vol. ii. p. 367.

† Phil. Trans. A. vol. excix. 1902, p. 55.

but that of minimum elastic after-effect, and preliminary observations of the deflexion showed that there was a gradual increase of the reading, reaching a limiting value according to the expression

$$y = A + Be^{-ct}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $y$  represents the distance from an arbitrary origin at the time  $t$  after producing a given deflexion, and  $A$ ,  $B$ , and  $C$  are constants. This means that there is a slow decrease in the controlling couple, and as the measurement of this couple depends on the observations of the period of small oscillations of the suspended system, it is necessary to obtain the instantaneous value for a deflexion reading taken at a given time after its production. A formula has been obtained which enables the deflexion observation for a Weber electro-dynamometer to be obtained to within one part in 40,000.

### *Theoretical Considerations.*

In order to calculate the magnitude of the creep at a given time after producing a deflexion, it is necessary that the wires should be in a known elastic state, and also that it should be possible to prepare the experiment and take readings at both extremities any number of times, at the same time maintaining the biflars in known condition. It will be seen that for most purposes it is sufficient to obtain a solution of the following problem :—

“Given a system supported by a suitable bifilar suspension (adjusted for use according to Gray\*), upon which a constant external couple can be applied in either direction, it is required to find the equation representing the creep after the deflexion has been reversed every  $T$  minutes for a comparatively long period, and to express this with reference to the instantaneous position of the first deflexion.”

Certain assumptions can be made, which are suggested by the form of equation (1), and also by the known fact that the behaviour of elastic after-effects is analogous to that of electric absorption in condensers.

Assume for the first deflexion that the rate of creep is proportional to the distance from an asymptotic value, and that subsequently the creep is complicated by the after-effects of deflexions made first in one direction and then in the other. If the wires have been at rest for a long time

\* Gray's ‘Absolute Measurements in Electricity and Magnetism,’ vol. i. p. 242.

their condition is approximately normal, and we have a definite static controlling couple. Suppose a deflexion is now produced. The instantaneous steady deflexion, if it could be read, would depend on the known static controlling couple of the bifilars, but immediately subsequent to the deflexion the structure of the wire gradually changes under the strain, the couple consequently decreases, and we get an increase of the deflexion. We can therefore, according to our initial assumption, express this creep in the form

$$\frac{dy}{dt} = k(D - y), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $y$  is the distance from the instantaneous deflexion at any time  $t$ ,  $D$  represents the distance of the asymptotic limit from this origin, and  $k$  is the proportionality constant which will depend on the torsional rigidity of the material, and upon the dimensions of the system.  $D$  will depend on the magnitude of the deflexion. Now suppose after the creep has proceeded a certain distance, that the deflexion is reversed by the same force applied in the opposite direction. Assume that the reversal may be made instantaneously. The rate in this case will be increased, as not only do we have the original movement, but there is also a recovery creep to be added on. If the suspension had been allowed to come to the undeflected position, the recovery would take place according to the law represented by

$$\frac{dz}{dt} = -kz, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $z$  is the distance from the undeflected original position; hence we may assume that the part of the creep due to the recovery can be represented by

$$\frac{dy}{dt} = -ky. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Upon any reversal of the deflexion we shall always have a rearrangement of the structure of the wire in the opposite direction to what it was before. In the special case of this problem, we may assume that the recovery part of the curve will always be given by equation (4). If now we solve equations (2) and (4), and equate  $x$  to the sum of the two results for  $y$ , we obtain the equation for a curve which shows the behaviour of any final creep, where  $x$  is the distance from the initial instantaneous deflexion, or from its equivalent in the opposite direction. In order to do this we must know

the "boundary conditions." This involves a knowledge of all the subsequent periods of reversal. In the case of our problem the solution is simple. If the force causing the deflexion is kept the same in magnitude, no matter which way it acts, and if the reversals are made every  $T$  minutes for  $n$  times, we get, from equation (2), that

$$y = D + ae^{-kt}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where  $a$  is the constant of integration, and solving equation (4) we get

$$y = be^{-kt}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $b$  is the constant of integration. Hence

$$\begin{aligned} x &= D + ae^{-kt} + be^{-kt} \\ &= D + ce^{-kt}, \end{aligned}$$

where  $c = a + b$ .

Let  $x_1$  be the distance from the origin at the time  $T$  of the first reversal; let  $x_2$  be the distance from the alternative origin at the time of the second reversal, and so on up to  $x_n$ , which is the distance from the origin at the time of the  $n$ th reversal.

If the deflexion has been reversed  $n-1$  times, we have

$$x = -x_{n-1}, \quad \text{when } t=0,$$

therefore

$$c = -x_{n-1} - D.$$

Hence

$$x = D(1 - e^{-kt}) - x_{n-1}e^{-kt}, \quad . \quad . \quad . \quad . \quad (7)$$

where  $x_{n-1}$  has still to be determined.

Now from equation (7) we see that

$$x_n = D(1 - e^{-kT}) - x_{n-1}e^{-kT},$$

and

$$x_1 = D(1 - e^{-kT}),$$

wherefore, by repeated transformations, we get

$$x_{n-1} = D(1 - e^{-kT}) [1 - e^{-kT} - e^{-2kT} - \dots + (-1)^n e^{-(n-2)kT}].$$

Since  $k$  and  $T$  are both positive the series is convergent, and we have

$$x_{n-1} = D(1 - e^{-kT}) \frac{1 - (-e^{-kT})^{n-1}}{1 + e^{-kT}},$$

and since we are considering the case  $nT$  large compared with  $T$ , we may take

$$x_{n-1} = D \frac{1 - e^{-kT}}{1 + e^{-kT}},$$

and equation (7) becomes

$$\begin{aligned} x &= D(1 - e^{-kt}) - D \frac{1 - e^{-kT}}{1 + e^{-kT}} e^{-kt} \\ &= D - D \frac{2}{1 + e^{-kT}} e^{-kt}, \quad \dots \dots \dots (8) \end{aligned}$$

which is the solution of our problem. Referred to the asymptotic limit as origin, this takes the form

$$x = -D \frac{2}{1 + e^{-kT}} e^{-kt}. \quad \dots \dots \dots (9)$$

It is important to note that in the distortion of bifilar suspensions under the conditions of ordinary deflexion measurements we are dealing with the structural alterations that occur at the beginning of what proves to be a group of several types of change. It has been pointed out by Trouton and Rankine, for the case of single wires\*, that there is first an immediate effect, which is followed by an increase with time; the latter may initially be considerable, but gradually diminishes to a small constant value. They refer to the first as the "primary strain," to the final constant rate as the "viscous flow," and to the intermediate effect as the "secondary strain." In single suspensions subjected to large distortions, the primary strain is often great, and it is difficult to examine experimentally because it takes place so rapidly, hence it has been with the subsequent behaviour under the secondary strain and viscous flow that most of the previous investigations have dealt. In the case of bifilar suspensions subjected to small distortions, we have the primary strain acting slowly over a much longer interval of time. We shall, therefore, not expect our result to hold for large values of  $t$  because our assumptions do not involve any cognizance of these later factors; but it does, however, suitably represent that range of the creep with which we have to deal in the practice and use of bifilar suspensions. When the viscous flow becomes appreciable, we find that the experimental curve lies above the theoretical curve (see fig. 2), and if the suspension be given time enough to recover from the primary strain, we find that there is left a considerable permanent distortion. These latter effects appear to cause a decrease in the couple approximately inversely proportional to the time, and can therefore be represented by an equation of the form

$$x = a + b \log t. \quad \dots \dots \dots (10)$$

\* Trouton and Rankine, *Phil. Mag.* vol. viii. 1904, p. 538.

By proper choice of constants we could get a more or less empirical formula of this type which would cover a very large range, but it is obviously impossible to apply such a formula to the early part of the creep, as it would involve the assumption that  $x$  was infinite when  $t$  was zero.

It might be suggested that the formula

$$y = a + b \log (1 + ct), \quad . \quad . \quad . \quad (11)$$

could be applied to express the whole range of the creep in agreement with analogous effects in electric absorption\*. Any particular creep can be expressed empirically by this formula over a very large range, but it was not found advantageous to develop an expression along these lines for the special case of our problem. For, supposing we take this equation as representing the initial creep, then by superposition of effects we get for the solution to our problem

$$y = b \log (1 + ct') - 2b \log (1 + \overline{ct' - T}) + 2b \log (1 + \overline{ct' - 2T}) - \dots + (-1)^n 2b \log (1 + \overline{ct' - nT}), \quad . \quad . \quad (12)$$

where  $a = 0$ , since we take  $y = 0$  when  $t = 0$ , and  $t' =$  the time from the start of the initial creep. If  $t$  equals the time from the  $n$ th reversal, then by putting  $t' = t + nT$  we get

$$y = b \log (1 + \overline{ct + nT}) - 2b \log (1 + \overline{ct + (n-1)T}) + 2b \log (1 + \overline{ct + (n-2)T}) - \dots + (-1)^n 2b \log (1 + \overline{ct}). \quad . \quad . \quad (13)$$

Now assuming the equation

$$y = D + ae^{-kt},$$

where  $a = -D$ , for the initial creep, since we take  $y = 0$  when  $t = 0$ , we get by the same method as the above

$$y = D(1 - e^{-kt'}) - 2D(1 - e^{-k(t' - T)}) + 2D(1 - e^{-k(t' - 2T)}) - \dots + (-1)^n 2D(1 - e^{-k(t' - nT)}), \quad . \quad . \quad (14)$$

and putting  $t' = t + nT$  we get

$$y = D(1 - e^{-k\overline{t + nT}}) - 2D(1 - e^{-k\overline{t + (n-1)T}}) + \dots + (-1)^n 2D(1 - e^{-kt}), \quad . \quad . \quad (15)$$

which reduces at once to equation (8) when  $nT$  is large compared with  $T$ . It is to be noted that we have here a much more concise development of equation (8). The former method was presented as offering a closer insight into the

\* H. A. Wilson, Proc. Roy. Soc. A. vol. lxxxii. p. 417 (1909).

actual process of the problem. A comparison of (13) and (15) shows that the former equation is much more cumbersome to deal with than the latter, and as equation (8) is so compact, and holds over that range for which it is necessary in practice for the correction of deflexion readings, we consider it therefore preferable.

*Methods of Observation.*

The suspension with which these experiments have to deal will carry a current of half an ampere without changing the period of vibration of the supported system by more than one part in 50,000, and will remain constant for weeks to the same degree of accuracy. The following observations on the period, which were recorded on a chronograph controlled from the McGill Observatory, illustrate this constancy:—

	Period.
I. No current flowing.....	11·6672 seconds
Current of half an ampere ...	11·6669   ,,
No current flowing.....	11·6669   ,,
Current of half an ampere...	11·6669   ,,
II. (Slight change in weight of system)	
No current flowing.....	11·6571   ,,
Current of half an ampere...	11·6574   ,,
No current flowing.....	11·6575   ,,
Current of half an ampere...	11·6573   ,,
III. May 5, 1910 .....	11·6566   ,,
" 28,   " .....	11·6564   ,,
June 3,   " .....	11·6564   ,,
" 13,   " .....	11·6564   ,,
IV. (Moment of inertia changed, but no change in weight of system.)	
Aug. 2, 1910 .....	6·5659   ,,
Nov. 14, 1910 .....	6·5652   ,,

The elastic fatigue produced by the continuous torsional oscillation\* in the determination of these periods was not of a sufficient magnitude to appreciably affect these observations in any way.

The deflexions were produced by passing a current through the dynamometer. This current passed through a constant resistance in an oil-bath, and it was arranged that the drop

\* Kelvin, *Encycl. Brit.* Art. "Elasticity," § 30.



in potential across this differed from the electromotive force of a normal Weston cell by only a few millionths of a volt. The cell was one of a number constructed according to the specifications of Wolff and Waters, and kept in a thermostat at a temperature of  $25^{\circ}\text{C}$ . constant to  $\cdot 01^{\circ}\text{C}$ .<sup>\*</sup> By opposing these two potential differences and measuring their difference on an ordinary potentiometer, with a sensitive galvanometer in the circuit, it was possible to adjust the current to a constant value. This was done by means of special rheostats capable of very delicate adjustment in the main circuit. It was not necessary to always adjust the current in order to obtain a given reading, for if the difference on the potentiometer was read, the value of the current could always be expressed in terms of that current which would produce a zero difference between the E.M.F. of the cell and the drop in potential across the resistance. Observations of the deflexion were taken simultaneously with a potentiometer reading, which never exceeded 700 microvolts, and was usually less than 100. As this variation is so small and could itself be obtained to better than 2 microvolts, it was always possible to apply to the deflexion a correction which could not be in error by as much as  $\cdot 001\text{ cm.}$  on the scale. For example, if the drop in potential was 100 microvolts greater than the E.M.F. of the Weston cell, then the current would have to be cut down one part in 10189 to get the value which would produce the same drop in potential as the Weston cell. As the circuits connecting the fixed and suspended coils of the dynamometer were connected in parallel (the resistance being in the suspended coils circuit), and as the deflexion varies with the product of the two currents, we see that the deflexion will be reduced by two parts in 10189, or in our case where the readings all lie between 42.3 and 42.4 cm. the correction would be  $\cdot 0083\text{ cm.}$  We could thus determine this more closely than we could read our scale, and were able to save considerable time and trouble in regard to keeping the current absolutely constant.

The telescope and scale arrangements (also described by Callendar†) enabled the deflexion to be obtained to  $\cdot 002\text{ cm.}$ , but as it was necessary to take readings at definite intervals during the creep, occasional uncertainties of as much as  $\cdot 005\text{ cm.}$  might arise, which were due to the necessity of bringing the suspension absolutely to rest before reading. This was performed by means of a special damping device, which made it possible to produce the deflexion and bring it

<sup>\*</sup> Wolff and Waters, *Bull. Bur. Stan.* vol. iv. 1907, p. 1; and Bronson and Shaw, *British Assoc. Report*, 1909, p. 396.

† *Loc. cit.*

TABLE I.—Observations for T=1.

	Time after reversal.	Series 1.			*Series 2.			*Series 3.			
Dynamometer reading in centimetres ...	1 min.	92-400	92-408	92-405	92-400	92-410	92-385	92-390	92-705	92-705 92-670	* 92-630 92-642
Potentiometer " microvolts ...		+240	+310	+240	+510	+540	+230	+270	+690	+650 +260	-180 +0
Corrected		92-380	92-382	92-385	92-357	92-365	92-366	92-367	92-648	92-651 92-648	92-645 92-642
Dynamometer reading in centimetres ...	2 "	92-405	92-406	92-412	92-400	92-410	92-380	92-395	92-715	92-705 92-675	92-650 92-635 92-650
Potentiometer " microvolts ...		+200	+190	+300	+380	+450	+120	+180	+670	+540 +210	-50 -200 -30
Corrected		92-383	92-390	92-387	92-368	92-373	92-370	92-380	92-659	92-660 92-658	92-654 92-652 92-652
Dynamometer reading in centimetres ...	3 "	92-415	92-412	92-420	92-415	92-375	92-395	92-395	92-722	92-680 92-655	92-638 92-650
Potentiometer " microvolts ...		+170	+150	+300	+360	+20	+110	+630	+180	-100 -260	-130
Corrected		92-401	92-400	92-394	92-398	92-380	92-370	92-386	92-679	92-665 92-663	92-660 92-661
Dynamometer reading in centimetres ...	4 "	92-418	92-410	92-425	92-418	92-380	92-390	92-390	92-725	92-675 92-675	92-665 92-645
Potentiometer " microvolts ...		+150	+140	+300	+240	+0	+40	+590	+60	+30	+0 -220
Corrected		92-406	92-398	92-399	92-402	92-380	92-380	92-387	92-676	92-670 92-673	92-665 92-663
Dynamometer reading in centimetres ...	5 "	92-420	92-424	92-435	92-423	92-402	92-380	92-390	92-728	92-675	92-660 92-668 92-641
Potentiometer " microvolts ...		+140	+170	+320	+220	+180	-110	-30	+580	+0	-200 -30 -300
Corrected		92-408	92-410	92-408	92-405	92-487	92-389	92-392	92-680	92-675	92-677 92-670 92-666
Dynamometer reading in centimetres ...	6 "	92-425	92-420	92-435	92-430	92-402	92-388	92-388	92-730	92-672 92-680	92-640
Potentiometer " microvolts ...		+110	+150	+300	+220	+120	-120	-120	+520	-60 +50	-330
Corrected		92-416	92-408	92-410	92-412	92-392	92-398	92-398	91-687	92-675 92-676	92-668
Dynamometer reading in centimetres ...	7 "	92-425	92-423	92-435	92-433						
Potentiometer " microvolts ...		+80	+150	+280	+210						
Corrected		92-418	92-411	92-413	92-416						

\* The change in these values is only due to change in arrangement of circuit, and does not affect the determination.

to rest within twenty seconds. In order to eliminate these errors, it was necessary to take the mean of a number of observations on any creep under the same repeated conditions.

Below are the series of observations of the creep for various values of  $T$ . In Table I. the full set of original observations are given in order to illustrate the method of procedure in calculating the mean values. For other values of  $T$  the results were obtained in exactly the same way, and merely the mean sets are shown.

Between the determination of each of the columns, the suspension was allowed to rest, and then the deflexion was again produced and reversed every minute a large number of times, in order to eliminate the effects of the previous seven or eight minutes' distortion.

To determine the constants  $k$  and  $D$  it is convenient to calculate the successive differences in each case, and then take the average of these. Let  $\chi_r$  mean the dynamometer reading when  $t=r$  minutes after the last reversal, and we get the following average values for the creep when  $T=1$  from Table I.:—

$$x_2 - x_1 = \cdot 009 \text{ cm.}$$

$$x_3 - x_2 = \cdot 008 \quad ,,$$

$$x_4 - x_3 = \cdot 005 \quad ,,$$

$$x_5 - x_4 = \cdot 005 \quad ,,$$

$$x_6 - x_5 = \cdot 004 \quad ,,$$

For the various values of  $T$  we get in exactly the same way all the results in Table II. In the cases of  $T=2$  and  $T=7$ , only a few sets were taken. At the foot of each column is a figure representing the relative weight of each series.

TABLE II.

Observations for	$T=1/2$ .	$T=1$ .	$T=2$ .	$T=5$ .	$T=7$ .	$T=9$ .
$x_2 - x_1$ .....	$\cdot 007$	$\cdot 009$	$\cdot 011$	$\cdot 013$	$\cdot 014$	$\cdot 014$
$x_3 - x_2$ .....	$\cdot 006$	$\cdot 008$	$\cdot 007$	$\cdot 011$	$\cdot 011$	$\cdot 010$
$x_4 - x_3$ .....	$\cdot 004$	$\cdot 005$	$\cdot 006$	$\cdot 008$	$\cdot 005$	$\cdot 007$
$x_5 - x_4$ .....	$\cdot 004$	$\cdot 005$	} $\cdot 010^*$	...	$\cdot 004$	$\cdot 006$
$x_6 - x_5$ .....	$\cdot 003$	$\cdot 004$		...	$\cdot 007$	$\cdot 005$
$x_7 - x_6$ .....	...	...	...	...	...	$\cdot 004$
$x_8 - x_7$ .....	...	...	...	...	...	$\cdot 004$
Weight .....	(2)	(3)	(1)	(2)	(1)	(3)

\* This value is for  $x_6 - x_4$ .

A rough graphical examination showed that the creeps could be represented by formula (8) with the proper value of  $T$  inserted. An algebraic method of calculation was adopted so that a full advantage of the observations might be taken. If we denote  $\log(x_{r+1}-x_r)$  by  $y_r$  for a given value of  $T$  we can represent each column of Table II. by the equation

$$y = m(r-1) + A_T,$$

where

$$m = \log(e^{-k})$$

and

$$A_T = \log(x_2 - x_1)$$

for the value of  $T$  considered. It will give a sufficiently accurate result for the best possible values of  $k$  and  $D$  if we find the best representative values for  $m$  and  $A_T$ , which will fit each of the series of equations in

$$y_1 = 0 \cdot m + A_T$$

$$y_2 = 1 \cdot m + A_T$$

$$y_3 = 2 \cdot m + A_T$$

$$\vdots$$

$$y_r = (r-1)m + A_T.$$

By applying the method of Gauss it can be shown that the desired values of  $m$  and  $A_T$  are given by a solution of the two equations

$$[y_1 + y_2 + y_3 + \dots + y_r] = [1 + 2 + 3 + \dots + (r-1)]m + rA_T$$

and

$$[y_2 + 2y_3 + 3y_4 + \dots + (r-1)y_r] = [1^2 + 2^2 + 3^2 + \dots + (r-1)^2]m + [1 + 2 + 3 + \dots + (r-1)]A_T.$$

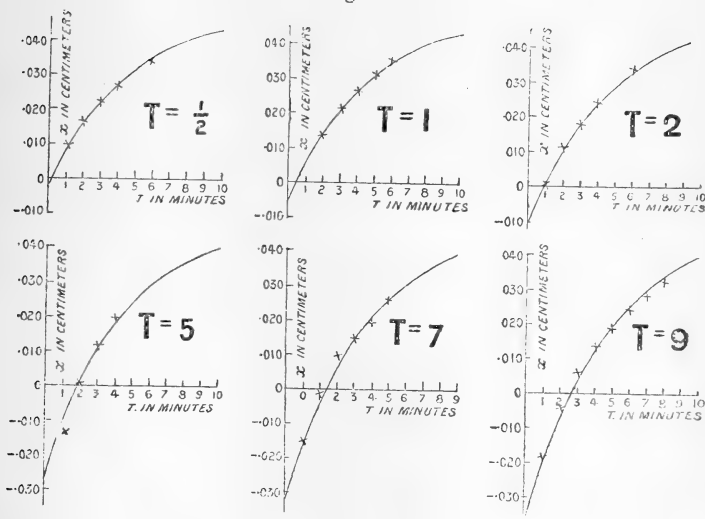
If we solve these for each column in Table II. we can get  $m$  and  $A_T$ , and hence the  $k$  and  $D$  which will best fit each set. If formula (8) holds we should get the same values for  $k$  and  $D$  throughout. (It should be noted that  $A_T$  is, of course, necessarily different in every case, but  $D$  calculated from  $A_T$ ,  $m$ , and  $T$  should be constant.) Table III. gives the results of this calculation.

TABLE III.

	$k$ .	D.	Weight.
$T=1/2$ .....	·21	·043	(2)
$T=1$ .....	·21	·053	(3)
$T=2$ .....	·22	·057	(1)
$T=5$ .....	·24	·052	(2)
$T=7$ .....	·24	·042	(1)
$T=9$ .....	·21	·045	(3)
Mean .....	·22	·049	

A set of curves for equation (8) with the above mean values of  $k$  and  $D$  are shown in fig. 1. The crosses represent the experimental results, and show how closely our results agree with the theoretical curves. For  $T=1/2$  quite an

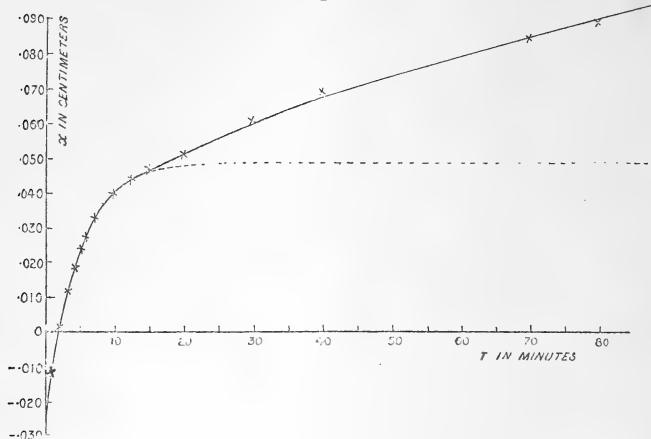
Fig. 1.



appreciable error may have been introduced by assuming the time of reversals to be instantaneous, and in the case of  $T=9$  the early creep is so rapid as to render it difficult to get the first two points in time.

In fig. 2 an experimental curve for  $T=5$  is drawn to show the form of creep over a longer range. It will be

Fig. 2.



seen that it is only during the primary strain that equation (8) holds, the latter part of the curve being of the type

$$y = a + b \log t;$$

the dotted line represents the theoretical curve (8), which is identical with the experimental curve for the first fifteen minutes.

### *Conclusions.*

Our results indicate that deflexion measurements which involve the use of bifilar suspensions can be performed with an increased accuracy.

An examination of the deflexion variation of this suspension during the first few minutes after producing a distortion, shows that the creep can be represented by a curve of the type

$$y = A + Be^{-Ct}$$

(where  $B$  can be expressed in terms of  $A$  and  $C$ ), although later the character of the movement alters, and is represented by

$$y = a + b \log t.$$

This shows that it is at first proportional to the distance from an asymptotic value, and later proceeds approximately inversely proportional to the time. It is chiefly with the first part of the curve, during the primary strain, that we have to deal in the case of bifilar suspensions, when seeking a

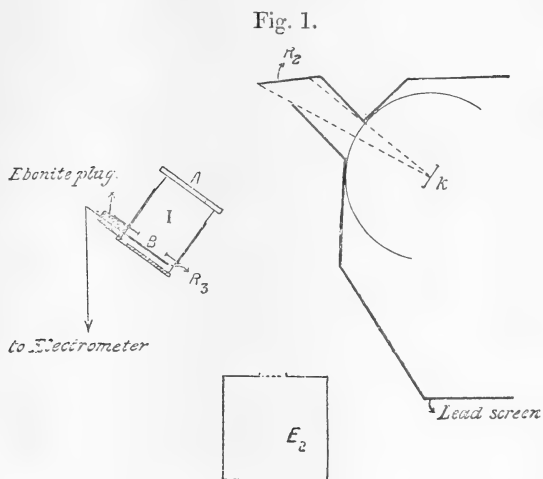
correction formula, thus the proper choice of experimental conditions enables a simple formula to be developed, from which the necessary corrections for after-effects can be definitely determined.

The testing of bifilar suspensions and the determination of the necessary constants can be performed by a method which is free from experimental difficulty.

It is a pleasure to record great indebtedness to Prof. H. T. Barnes for his many suggestions and kind interest in the work.  
March 6, 1911.

XLIII. *The Transformation of the Energy of Homogeneous Röntgen Radiation into Energy of Corpuscular Radiation.*  
By CHARLES A. SADLER, D.Sc., Oliver Lodge Fellow in the University of Liverpool\*.

IN a recent paper† the author gave an account of an investigation of the corpuscular radiation from metals excited by beams of homogeneous Röntgen radiation. The following is an account of some further deductions derived from the results of these experiments.



For the sake of clearness a diagrammatic representation of the apparatus then used is given in fig. 1.

\* Communicated by the Author. Part of the expenses connected with this Research were defrayed by a Government Grant.

† Sadler, Phil. Mag. March 1910.

Radiation from an ordinary X-ray bulb falling upon the radiator  $R_2$  excited a beam of homogeneous secondary X rays whose absorption coefficient by aluminium was known. This homogeneous beam passed through the apertures A and B in the ionization-chamber I, and fell upon the radiator  $R_3$ , which served as a source of corpuscular radiation.

The aperture B was covered by a thin sheet of aluminium which also gave off corpuscular radiation usually of small intensity. This latter radiation could be allowed for, and thus the corpuscular radiation from the radiator  $R_3$  determined.

Let us consider the case when corpuscular radiation is emitted in a normal direction by such a plate as  $R_3$ , upon which a uniform parallel beam of homogeneous Röntgen radiation falls perpendicularly. The Röntgen radiation passing across the space of the ionization-chamber between the aperture B and the radiator  $R_3$  is absorbed to a certain extent by the air. If the distance between B and  $R_3$  be made 1 cm., then if  $I_0$  be the energy passing per second through unit area of the window B whose area is S, the absorption per second of the energy of the secondary beam by the air of the ionization-chamber is given by

$$I_0(1 - e^{-\lambda_2})S,$$

where  $\lambda_2$  is the absorption coefficient in air of the secondary beam.

It was pointed out in a previous paper\* that the ionization produced in a given volume of air traversed by a beam of homogeneous Röntgen radiation is approximately proportional to the absorption of that radiation by the air through which it passes. We may, therefore, write for the ionization in this case

$$C I_0(1 - e^{-\lambda_2})S,$$

where C is a constant.

Turning now to the corpuscular radiation excited by the secondary Röntgen beam, we may define the quantity  $k$  such that the fraction of the energy of the incident secondary Röntgen beam passing normally through a thin layer of the radiator  $R_3$  of thickness  $\delta x$  which is transformed into energy of corpuscular radiation is  $k \delta x$ .

If  $I'$  be a measure of the energy of the secondary Röntgen beam passing normally per second through unit area of the tertiary radiator at a depth  $x$  below the surface, the fraction

\* Sadler, Phil. Mag. July 1909.



of this energy converted per second into energy of corpuscular radiation is  $I'k\delta x$ .

The corpuscular energy entering the ionization-chamber I from a layer of thickness  $\delta x$  and of area S (the area of  $R_3$  upon which the secondary radiation falls) situated at a depth  $x$  below the surface of  $R_3$

$$= \frac{\omega}{4\pi} S I' \delta x e^{-\beta_1 x}, \quad . . . . . (2)$$

where  $\beta_1$  is the absorption coefficient of the corpuscular radiation by the material of the tertiary radiator, and  $\omega$  is the mean solid angle subtended by the ionization-chamber at a point in the layer at which a corpuscle originates (the value of  $\omega$  will not appreciably alter with changes in value of  $\beta_1$ ).

But  $I' = I e^{-\lambda_1 x}$ , where I is the energy of the homogeneous Röntgen radiation incident per sec. upon unit area at the surface of the radiator  $R_3$ , and  $\lambda_1$  the coefficient of absorption of the incident radiation by the material of the tertiary radiator.

The whole energy passing into the ionization-chamber is then given by

$$\int_0^\infty \frac{\omega}{4\pi} k I S \delta x e^{-(\beta_1 + \lambda_1)x}. \quad . . . . . (3)$$

On integration this becomes

$$\frac{\omega}{4\pi} \frac{S I k}{\beta_1 + \lambda_1}, \quad . . . . . (4)$$

or since we have  $I = I_0 e^{-\lambda_2}$ , this expression for the energy entering the ionization-chamber per sec. may be written

$$\frac{\omega}{4\pi} \frac{S I_0 k e^{-\lambda_2}}{\beta_1 + \lambda_1}. \quad . . . . . (5)$$

Since none of the corpuscles can travel more than a few mm. in air it may be assumed that the ionization which they produce in the space between  $R_3$  and B will be proportional to the total energy of the corpuscles emerging from the radiator  $R_3$ . We may, therefore, write for the total ionization produced by the corpuscles

$$D \frac{\omega}{4\pi} \frac{S I_0 k e^{-\lambda_2}}{\beta_1 + \lambda_1}, \quad . . . . . (6)$$

where D is a constant.

The ratio of the total ionization per sec. due to the corpuscular radiation to that produced by the exciting homogeneous Röntgen radiation per sec. in 1 cm. of air

$$= D \frac{\omega}{4\pi} \frac{S I_0 k e^{-\lambda_2}}{\beta_1 + \lambda_1} \bigg/ C I_0 S [1 - e^{-\lambda_2}], \quad . \quad . \quad (7)$$

$$= E k \frac{e^{-\lambda_2}}{(1 - e^{-\lambda_2})(\beta_1 + \lambda_1)} = R \text{ say, } . \quad . \quad . \quad (8)$$

where E is written for  $\frac{D}{C} \frac{\omega}{4\pi}$ ,

and therefore

$$k = \frac{R}{E} (\beta_1 + \lambda_1) (e^{\lambda_2} - 1), \quad . \quad . \quad . \quad (9)$$

No information is at present available for a determination of either C or D.

In the former paper a method, by which the determination of R could be obtained, was described. It was pointed out that a correction was necessary to allow for the ionization produced by the tertiary Röntgen radiation from  $R_3$  (that from the aluminium window being small in comparison).

The ratio determined was that of the total ionization produced by the corpuscular radiation from  $R_3$  to that produced by the secondary incident radiation and the tertiary radiation from  $R_3 = R'$  say. If, then, we find the ratio of the ionization produced by the secondary and tertiary radiation to that produced by the secondary alone  $= R''$ , and multiply these ratios together, we obtain the value of R of equation (8).

Let  $k'$  be a quantity such that the fraction of the incident energy of the secondary beam passing normally through a thin layer of the tertiary radiator of thickness  $\delta x$  which is transformed into tertiary radiation is  $k' \delta x$ . Then if  $\omega'$  be the mean solid angle subtended by the ionization-chamber at any point of the tertiary radiator,  $\lambda_3$  the absorption coefficient of the tertiary radiation in the material of which the radiator is composed, and  $\lambda_4$  the absorption coefficient in air, it can be shown that the ratio  $R_2'$

$$= 1 + \frac{\omega'}{4\pi} \frac{k'}{\lambda_1 + \lambda_2} \frac{(e^{\lambda_4} - 1)}{(e^{\lambda_2} - 1)} \frac{1}{e^{\lambda_4}}.$$

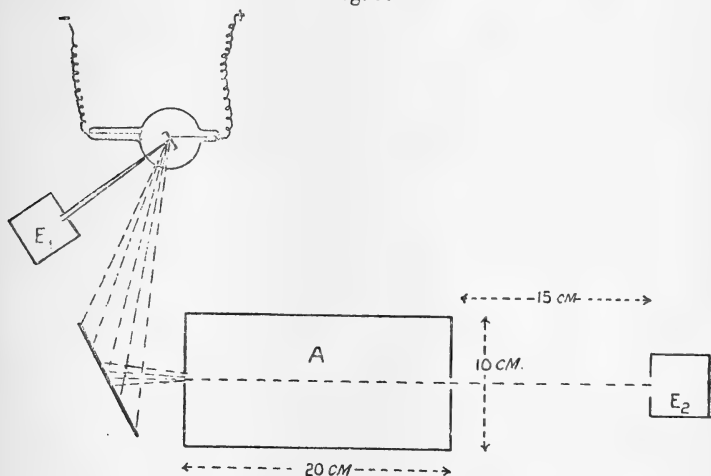
To determine the ratio  $R_2''$  plates of pure iron and copper of equal size and shape were alternately placed in the position  $R_2$  shown in fig. 1. This position could be reproduced with great accuracy. A plate of pure iron served as the tertiary radiator. The ratio of the ionizations produced in the chamber I and in the electroscope  $E_2$  were noted with the

iron and copper radiators respectively. The amount of tertiary radiation excited by the radiation from either copper or iron in  $E_2$  was negligible, since the vessel was lined with aluminium. In the ionization-chamber I, however, copper radiation readily excited tertiary radiation in the iron, while the radiation from iron excited little or none. The ratio when iron was used as secondary radiator will give us a measure of the ratio which would be obtained with copper as secondary radiator if no tertiary radiation were excited in the iron. The actual ratio when copper is used as secondary gives a measure of the ionization due to the secondary from copper, together with that due to the tertiary from iron. This latter ratio divided by the former gives the value of  $R_2''$ .

The mean of several determinations, all of which agreed among themselves very closely, gave 1.045 as the corrected value for  $R''$ .

Substituting in equation (10) the value of  $\omega'$  was found to  $\approx 2.00$ . Most of the values of  $k'$  and  $\lambda_1$  and  $\lambda_2$  were taken from a previous paper, a few, however, being specially determined. The method of measuring these absorption coefficients  $\lambda_2$  and  $\lambda_4$  was as follows. A stout brass cylindrical vessel A, 20 cm. long, in the centre of each end of which was drilled a hole 1.0 cm. diameter, which was afterwards covered with thin aluminium (.003 cm.), was placed with its axis along the line joining the centre of the radiator  $R_2$  to the centre of the window of the electroscope  $E_2$ , as shown in fig. 2.

Fig. 2.



The pressure of the air in A was reduced by connecting it to a water pump, the pressure being indicated by a mercury

gauge. A narrow pencil of the primary beam was passed into an electroscope  $E_1$ .

The ratio of the readings on the electroscopes  $E_2$  and  $E_1$  was taken at the ordinary pressure of the room, and again when the pressure of the air in the cylinder had been reduced to about 10 cm. of mercury, as indicated by the gauge.

We may express the air in the cylinder in each case in terms of a column of air of the same cross-section and pressure of 76 cm. of mercury at  $0^\circ$  C. Let these columns be of length  $L_1$  and  $L_2$ . The decrease in the ratio of the readings on the electroscopes  $E_2$  and  $E_1$  which occurred when the pressure was again made atmospheric, gave a measure of the absorption of this particular secondary radiation by a column of air of thickness  $L_1 - L_2$ , and thus the absorption coefficient in air at 76 cm. of mercury and  $0^\circ$  C. was determined. The values for copper and arsenic radiation were respectively  $\cdot 01127$  and  $\cdot 00536$ .

It had been shown in a paper\* on the absorption of Röntgen radiation that the ratio of the absorption coefficients of any two homogeneous beams is a constant for all absorbing substances, in which no tertiary radiation of the homogeneous type is excited by either of the beams under consideration. It was to be expected, therefore, that the ratio of the absorption coefficients in aluminium and air would be constant for beams from copper and arsenic. The ratio of the absorption coefficient in aluminium for these radiations given in the paper referred to is 2.12. The ratio of the coefficients in air given above is 2.10.

Taking advantage of this fact the absorption coefficients in air of the other secondary radiations used were deduced from the absorption coefficients in aluminium.

The values of  $R$  of equation (8) are tabulated below.

TABLE I.—Values of  $R$ .

Tertiary Radiators.	Metals which serve as the source of homogeneous secondary Röntgen Radiation.											
	Fe.	Co.	Ni.	Cu.	Zn.	As.	Se.	Sr.	Mo.	Rho.	Ag.	Sn.
Aluminium...	·007	·009	...	...	·018	·036	·048	·115	·264	·400	·500	·680
Iron .....	...	·013	·256	·262	·267	·287	·305	·322	·389	·514	·598	·710
Copper .....	...	...	...	·018	·0594	·386	·398	·406	·470	·563	·645	·746
Silver .....	·079	·098	·119	·148	·178	·333	·410	·672	·972	1·08	1·15	2·19

\* Barkla and Sadler, *Phil. Mag.* May 1909.

The values of  $\beta_2$ , the absorption coefficient of the corpuscular radiation in air, were given in a previous paper. The absorption coefficients of the corpuscular radiation in the material of the tertiary radiators were not measured directly. It is known that for soft  $\beta$  rays the absorption in different substances approximately obeys a density law. The corpuscles here dealt with correspond to very soft  $\beta$  rays, and may be expected to suffer absorption in a similar manner. But whatever law the absorption obeyed, it is probable that the ratio of the absorption coefficients in air of the corpuscular radiation excited by any two secondary X radiations is equal to the ratio of these absorption coefficients in a metal. Referring to the expression for  $k$  it will be seen that if  $\beta_1$  is large compared with  $\lambda_1$  (which in practice proves to be the case), then since we are chiefly concerned with the *relative* values of  $k$  for a particular tertiary radiator a knowledge of the actual values of  $\beta_1$  is not of great importance.

The values of the various absorption coefficients required in the above calculations are given in the following table.

TABLE II.

Secondary Radiator.	Values of $\lambda_1$ . Al as Absorber*.	Values of $\beta_2$ (mean†).	Values of $\lambda_3$ .	
			Fe as Absorber.	Cu as Absorber.
Iron .....	239	...	514	851
Cobalt .....	193.2	...	521	674
Nickel .....	159.5	38.9	2440	554
Copper .....	128.9	37.0	2030	474
Zinc .....	106.3	35.8	1715	497
Arsenic .....	60.7	30.1	1040	1575
Selenium .....	51.0	26.4	903	1340
Strontium .....	25.5	20.8	444	681
Molybdenum.....	13.1	15.3	273	417
Rhodium .....	8.44	10.7		
Silver .....	6.75	8.83	140	198
Tin .....	4.33	6.56	99.2	145

\* The values of  $\lambda_2$  and  $\lambda_4$  are obtained from the corresponding values of  $\lambda_1$  by multiplying by the factor .0000875.

† The values of  $\beta_1$ , the absorption coefficient of the corpuscular radiation in the material of the tertiary radiator, are obtained by multiplying the value of  $\beta_2$ , the absorption coefficient of the corpuscular radiation in air, by the factor  $\frac{\rho_1}{\rho_2}$ , where  $\rho_1$  is the density of the material of the tertiary radiator and  $\rho_2$  the density of air at 76 cm. of Hg and 0° C.

*Phil. Mag.* S. 6. Vol. 22. No. 129. Sept. 1911. 2 H

The relative values of  $k$  calculated on the above assumptions are given in Table III.

TABLE III.

Values of  $Ek$ , where  $E = \frac{D}{C} \cdot \frac{\omega}{4\pi}$ .

Radiators which act as the source of homogeneous secondary Röntgen Radiation.												
Tertiary Radiators.	Fe.	Co.	Ni.	Cu.	Zn.	As.	Se.	Sr.	Mo.	Rho.	Ag.	Sn.
Iron .....	21.6	53.9	850	669	545	278	218	90.1	39.4	24.5	18.8	10.7
Copper .....	25.3	...	...	52.2	137	430	325	125	56.0	30.8	23.1	12.8
Silver .....	584	555	536	510	491	436	395	256	141	70.1	48.8	44.6
Aluminium...	13.1	13.0	...	...	12.6	12.1	11.9	11.2	9.80	6.42	5.42	3.54

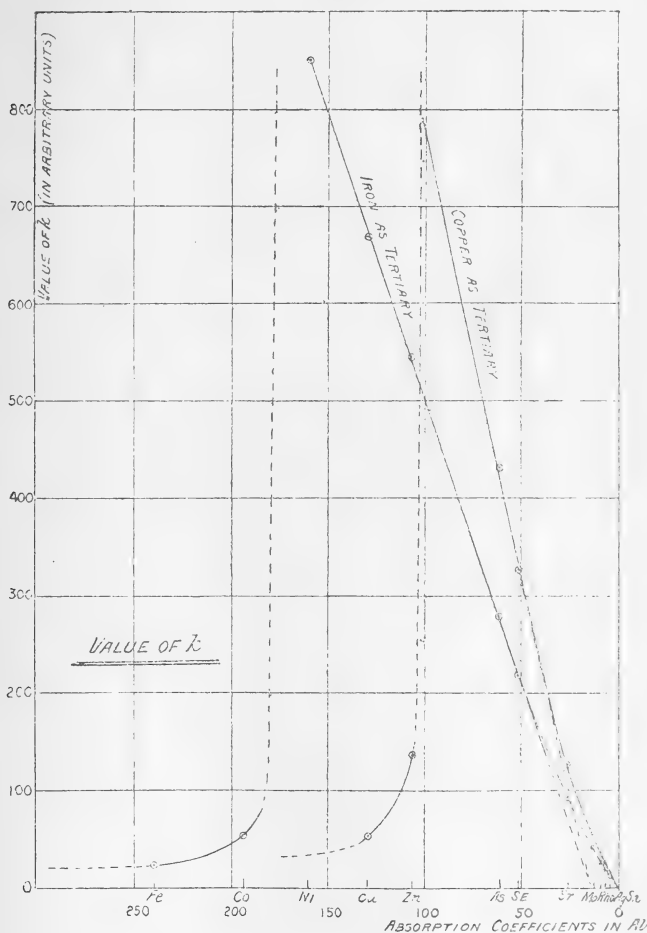
The corresponding values of $k'$ for Iron and Copper are												
Tertiary Radiators.	Fe.	Co.	Ni.	Cu.	Zn.	As.	Se.	Sr.	Mo.	Rho.	Ag.	Sn.
Iron .....	20.0	51.4	526	403	307	137	96.0	43.9	18.3	...	7.95	4.74
Copper .....	...	...	...	...	43.0	390	267	131	52	...	22.4	14.0

For either iron or copper as tertiary radiator, if we plot the values of  $k$  corresponding to any particular secondary exciting radiation against the absorption coefficients of the secondary radiation in aluminium, we get the curve shown in fig. 3.

It will be seen from the figure that for a given tertiary radiator  $R_3$  the value of  $k$  is very small for those secondary Röntgen radiations which are softer than that characteristic of  $R_3$ . When the secondary beam becomes just more penetrating an increase in the value of  $k$  is at once apparent, and for a beam very little more penetrating the value of  $k$  assumes a maximum value many times its previous one. For more penetrating beams the value of  $k$  decreases as a linear function of the penetrating power of the exciting radiation, while for more penetrating beams still the value of  $k$  decreases more slowly, approaching a zero value for an exceedingly penetrating beam. It is possible, however, that at some later stage a further corpuscular radiation would be emitted, when a similar sudden rise and subsequent fall in

the value of  $k$  would take place. An indication of this is seen in the values of  $R$  and  $Ek$  for silver as a tertiary radiator and tin as secondary.

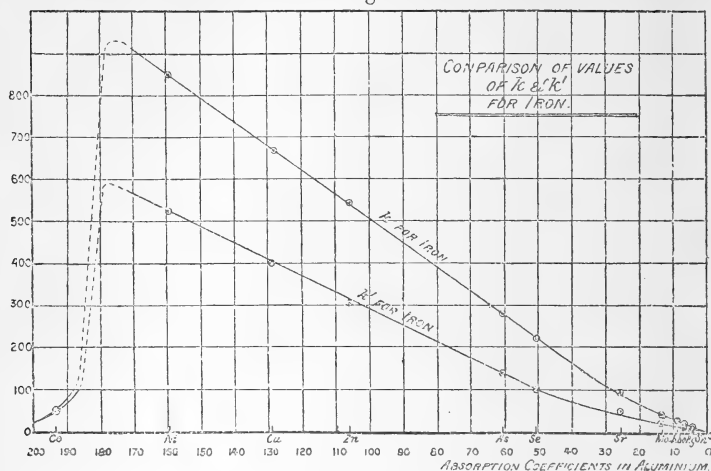
Fig. 3.



The similarity between the variations in the values of  $k$  for the corpuscular and  $k'$  for the tertiary Röntgen radiation from iron and copper is very striking. The increase in the values of  $k$  and  $k'$  to a maximum occurs suddenly in both cases, and for the same penetrating power of the secondary radiation. The values of  $k$  and  $k'$  then decrease in a similar

manner in each case. This is clearly shown in fig. 4, in which the values of  $k'$  for the tertiary radiation are taken from a previous paper supplemented by values recently obtained, the scale chosen for  $k$  and  $k'$  being quite arbitrary.

Fig. 4.



It is thus evident that a very close connexion exists between the emission of corpuscular radiation and the production of Röntgen radiation of the homogeneous type in the case of the group of elements Cr—Ag.

This is in entire agreement with the supposition advanced by various investigators that the production of Röntgen radiation is always accompanied by the emission of negative corpuscles.

We may even go further and say that there is strong evidence that whenever the characteristic radiation is excited there is always produced a strictly proportional amount of corpuscular radiation.

#### *Aluminium as Tertiary Radiator.*

In the case of aluminium it was found that traces of iron were present in every specimen that could be obtained, and although in the sample used iron was present only to the extent of .4 per cent., by weight, these traces increased the tertiary Röntgen radiation from aluminium to a considerable extent. Correcting for this iron radiation it was found that the radiation of the Röntgen type emitted by aluminium when used as a tertiary radiator was nearly all scattered radiation.

It has been stated by various experimenters that the radiation scattered by a substance of low atomic weight is of the same penetrating power as the incident radiation. Experiments now in progress seem to throw doubt on this statement.

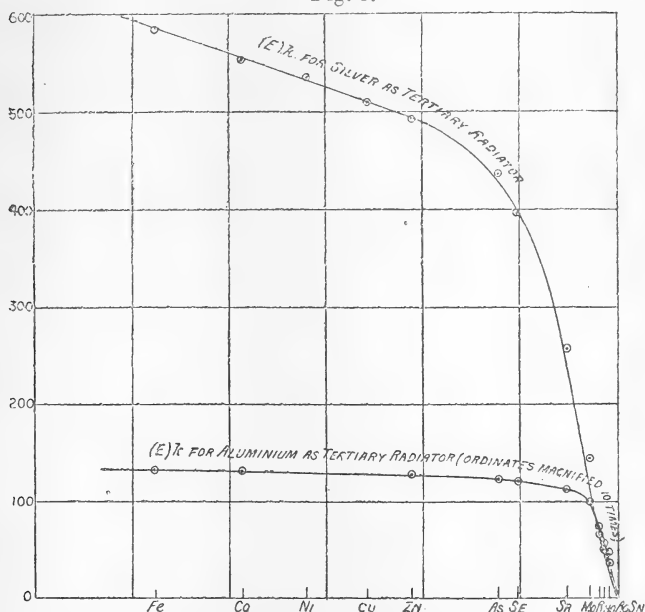


the scattered radiation appears to be very much softer than the incident radiation. With the evidence at present available it is not easy to decide whether this is due to an admixture of a feeble soft characteristic radiation or to a general softening of the entire beam in the process of scattering. The evidence, however, is much more in favour of the latter than the former.

When aluminium was used as a tertiary radiator a corpuscular radiation was always present. It has been shown that the amount of radiation scattered by a given mass of an element increases with the atomic weight of that element. In the case of the corpuscular radiation it will be seen from the second column of Table III. that the relative amounts of corpuscular radiation produced follow a similar law. (The exceptionally high values when silver is used as a tertiary are no doubt partly due to a special corpuscular radiation accompanying the production of the soft characteristic radiation of silver.)

Taken together these facts, though not in themselves conclusive, appear to suggest that corpuscles are shot out of a substance when it scatters Röntgen radiation, as well as when it emits a characteristic radiation.

Fig. 5.



The values of  $k$  for aluminium and silver are shown graphically in fig. 5.

A fuller discussion of these facts may with advantage be deferred until some further experiments on the scattered radiation, at present in progress, are completed.

A striking point is specially emphasized in the case of silver. It was pointed out in an earlier paper that the speed with which the corpuscles emerge from a radiator depended only upon the hardness of the exciting radiation, and not at all upon the material of which the radiator was composed. Consequently the speed does not depend at all upon the penetrating power of the Röntgen radiation characteristic of the tertiary radiator, even though the emission of the corpuscular radiation is evidently very intimately connected with the emission of this characteristic Röntgen radiation.

When the exciting beam is from tin ( $\lambda$  in Al = 4.33) both the soft and the hard characteristic radiations are emitted by silver. The ionization produced by the corpuscles accompanying the emission of hard tertiary X radiation is approximately equal to that produced by the corpuscles accompanying the soft X radiation. The curves giving the values of the absorption coefficient of the corpuscular radiation, consisting of these two systems of corpuscles, clearly indicated that the corpuscles emerged with the same velocity in either case, this velocity being the same as that with which corpuscles emerge from any of the other tertiary radiators when excited by the secondary radiation from tin.

In conclusion, I wish to thank Professor Wilberforce for the interest he has shown throughout these investigations.

I wish also to thank Mr. Mesham, M.Sc., for his assistance in carrying out some of the experiments.

The George Holt Physics Laboratories,  
June 30, 1911.

XLIV. *Non-Newtonian Mechanics*:—*The Direction of Force and Acceleration.* By RICHARD C. TOLMAN, Ph.D., Instructor in Physical Chemistry at the University of Michigan\*.

IF force is defined as the rate of increase of momentum, the equation

$$\mathbf{F} = \frac{d}{dt}(m\mathbf{u}) = m \frac{d\mathbf{u}}{dt} + \frac{dm}{dt}\mathbf{u} \quad . \quad . \quad . \quad (1)$$

allows for a change in mass as well as a change in

\* Communicated by the Author.

velocity. This is the fundamental equation of non-Newtonian mechanics\*.

It has been shown from the principle of relativity† that the mass of a moving body is given by the equation

$$m = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}},$$

where  $m_0$  is the mass of the body at rest and  $c$  is the velocity of light. Substituting in equation (1) we obtain

$$\mathbf{F} = \frac{d}{dt} \left( \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \mathbf{u} \right) = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \frac{d\mathbf{u}}{dt} + \frac{d}{dt} \left( \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \right) \cdot \mathbf{u}. \quad (2)$$

From an inspection of equations (1) and (2) it is evident that the force acting on a body is equal to the sum of two vectors, one of which is in the direction of the acceleration  $d\mathbf{u}/dt$  and the other in the direction of the existing velocity  $\mathbf{u}$ , so that *in general the force and the acceleration it produces are not in the same direction*. If the force which does produce acceleration in a given direction be resolved perpendicular and parallel to the acceleration, it may be shown that the two components are connected by a definite relation.

\* This definition of force was first used by Lewis (Phil. Mag. xvi. p. 705 (1908)). In Einstein's later treatment of the principle of relativity, *Jahrbuch der Radioaktivität*, iv. p. 411 (1907), he defines force by the equations

$$F_x = \frac{d}{dt} \left\{ \frac{m_0 u_x}{\sqrt{1 - \frac{u^2}{c^2}}} \right\}, \quad F_y = \frac{d}{dt} \left\{ \frac{m_0 u_y}{\sqrt{1 - \frac{u^2}{c^2}}} \right\},$$

$$F_z = \frac{d}{dt} \left\{ \frac{m_0 u_z}{\sqrt{1 - \frac{u^2}{c^2}}} \right\}.$$

He there states that this definition has in general no physical meaning. We see, however, that these are merely the scalar equations corresponding to equation (2) above and hence derivable from equation (1), which is an obvious definition of force and has a physical meaning. In further support of this definition of force, it has recently been pointed out by the writer, Phil. Mag. xxi. p. 296 (1911), that, combined with the principle of relativity, it leads to a derivation of the fifth fundamental equation of electromagnetic theory in its exact form

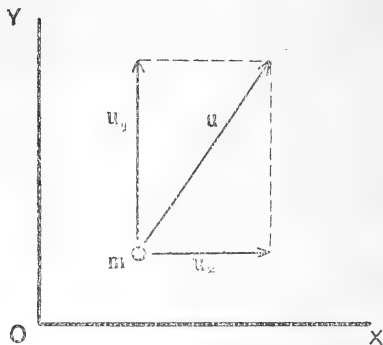
$$\mathbf{F} = \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{H},$$

there being no necessity for distinguishing between longitudinal and transverse mass.

† Lewis & Tolman, Proc. Amer. Acad. xlv. p. 711 (1909); Phil. Mag. xviii. p. 510 (1909).

*Relation between the Components of Force Parallel  
and Perpendicular to the Acceleration.*

Fig. 1.



Consider a body (fig. 1) moving with the velocity

$$\mathbf{u} = u_x \mathbf{i} + u_y \mathbf{j}.$$

Let it be accelerated in the Y direction by the action of the component forces  $F_y$  and  $F_x$ .

From equation (2) we have

$$F_x = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \frac{du_x}{dt} + \frac{d}{dt} \left( \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \right) \cdot u_x \quad \dots \quad (3)$$

$$F_y = \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \frac{du_y}{dt} + \frac{d}{dt} \left( \frac{m_0}{\sqrt{1 - \frac{u^2}{c^2}}} \right) \cdot u_y \quad \dots \quad (4)$$

Introducing the condition that there is no acceleration in the X direction, which makes  $du_x/dt = 0$ , further noting that  $u^2 = u_x^2 + u_y^2$ , by the division of equation (3) by (4) we obtain

$$\frac{F_x}{F_y} = \frac{u_x u_y}{c^2 - u_x^2},$$

$$F_x = \frac{u_x u_y}{c^2 - u_x^2} F_y \quad \dots \quad (5)$$

Hence in order to accelerate a body in a given direction, we may apply any force  $F_y$  in the desired direction, but must at the same time apply at right angles another force  $F_x$  whose magnitude is given by equation (5).

From a qualitative consideration, it is also possible to see the necessity of a component of force, perpendicular to the

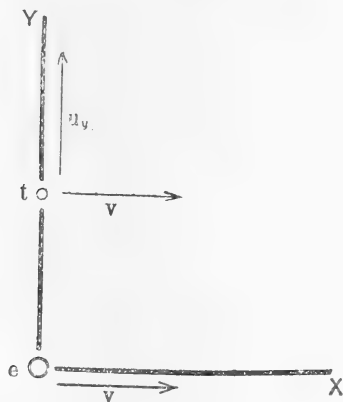
desired acceleration. Referring again to fig. 1, since the body is being accelerated in the  $Y$  direction, its total velocity and hence its mass are increasing. This increasing mass is accompanied by increasing momentum in the  $X$  direction even when the velocity in that direction remains constant. The component force  $F_x$  is necessary for the production of this increase in  $X$ -momentum.

In predicting the path of moving electrons with the help of the fifth equation of electromagnetic theory,  $\mathbf{F} = \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{H}$ , we find an interesting application of equation (5).

### Application in Electromagnetic Theory.

Consider a charge  $\epsilon$  constrained to move in the  $X$  direction with the velocity  $v$  and let it be the origin of a system of moving coordinates  $Y\epsilon X$  (fig. 2). Suppose now a test electron  $t$ , of unit charge, situated at the point  $x=0$ ,  $y=y$ ,

Fig. 2.



moving in the  $X$  direction with the same velocity  $v$  as the charge  $\epsilon$ , and also having a component velocity in the  $Y$  direction  $u_y$ . Let us predict the nature of its motion under the influence of the charge  $\epsilon$ .

The moving charge  $\epsilon$  will be surrounded by electric and magnetic fields whose intensities at any point are given by the following expressions \*, obtained by integrating Maxwell's

\* Abraham, *Theorie der Elektrizität*, vol. ii. p. 86 et seq. (B. G. Teubner, Leipzig and Berlin, 1908).

four field equations, for the case of a moving point charge,—

$$\mathbf{E} = \left(1 - \frac{v^2}{c^2}\right) \frac{\epsilon \mathbf{R}}{R^3 \left(1 - \frac{v^2}{c^2} \sin^2 \psi\right)^{\frac{3}{2}}} \dots \dots \dots (6)$$

$$\mathbf{H} = \frac{1}{c} \mathbf{v} \times \mathbf{E}, \dots \dots \dots (7)$$

where  $\mathbf{R}$  is the radius vector connecting the moving charge with the point in question and  $\psi$  is the angle between  $\mathbf{R}$  and  $\mathbf{v}$ .

For the field acting on the test electron  $t$ , situated at the point  $x=0$ ,  $y=y$ , we may substitute  $\mathbf{R} = y\mathbf{j}$  and  $\sin \psi = 1$ , giving us,

$$\mathbf{E} = - \frac{\epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \mathbf{j} \dots \dots \dots (8)$$

and

$$\mathbf{H} = \frac{v}{c} \frac{\epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \mathbf{k}, \dots \dots \dots (9)$$

substituting into the fifth fundamental equation of electromagnetic theory,

$$\mathbf{F} = \mathbf{E} + \frac{1}{c} \mathbf{v} \times \mathbf{H} \dots \dots \dots (10)$$

we obtain the force acting on the unit test electron  $t$ .

[Note in the above equation that  $\mathbf{v}$ , the velocity of the electron, is for our case  $v\mathbf{i} + u_y\mathbf{j}$ .]

$$\mathbf{F} = \frac{\epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \mathbf{j} - \frac{1}{c^2} \frac{v^2 \epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \mathbf{j} + \frac{1}{c^2} \frac{vu_y \epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \mathbf{i}, \quad (11)$$

or,

$$F_x = \frac{\epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \frac{vu_y}{c^2}, \dots \dots \dots (12)$$

$$F_y = - \frac{\epsilon}{y^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \left(1 - \frac{v^2}{c^2}\right) \dots \dots \dots (13)$$

Under the action of the component force  $F_x$  we might at first sight expect the electron  $t$  to acquire an acceleration in the X direction. Such a condition, however, would not be in agreement with the *principle of relativity*, since from the

point of view of an observer who is moving along with the charge  $\epsilon$ , the phenomenon is merely one of ordinary *electrostatic* repulsion and the test electron should experience no change in velocity in the X direction but should be accelerated merely in the Y direction.

If, however, we divide equation (12) by (13) we obtain

$$F_x = \frac{v_y}{c^2 - v^2} F_y, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

which agrees with equation (5), the necessary relation for zero acceleration in the X direction. The application of equation (5) thus removes a discrepancy which could not be accounted for in any system of mechanics in which force and acceleration are in the same direction.

### Summary.

For non-Newtonian mechanics, it has been pointed out that force and the acceleration it produces are not in general in the same direction. A definite relation (equation 5) has been derived connecting the components of force parallel and perpendicular to the acceleration. For a special problem, the application of this relation has removed an apparent discrepancy between the predictions based on the electromagnetic theory and on the principle of relativity.

Ann Arbor, Mich.

March 25th, 1911.

### XLV. Notices respecting New Books.

*The Principles of Electric Wave Telegraphy and Telephony.* By Prof. J. A. FLEMING, D.Sc., F.R.S. Second Edition. Pp. xviii + 906. With Illustrations. (London : Longmans, Green & Co. 1910.)

**A**LTHOUGH it is only five years since the first edition of this book appeared, yet, so vast have been the developments since its appearance, that this new edition is almost a new book. Those who are acquainted with Professor Fleming's previous treatises will be prepared for a masterly exposition of electric wave telegraphy; but he surpasses himself in his presentation of this subject. No one is better qualified than he for the task. Not only is he intimate with the mathematical and theoretical side of the subject; but he has for many years been in close contact with and has himself contributed largely to the rapid developments which have taken place both on the theoretic and experimental sides. It is impossible to do justice to this book in the space at our disposal—the enumeration of the headings of the chapters would almost exhaust it. The characteristic feature is the happy combination of theory with experiment, each being dealt with in an encyclopædic manner. For example, twelve pages deal with

interrupters for induction coils, one hundred pages with high-frequency electrical measurements, eighty pages with damping and resonance, forty-three with stationary electric waves on wires, seventy-seven with the theory of electromagnetic waves (including detailed diagrams by Hertz, Pearson and Lee, and Love of the lines of force of Hertzian oscillators under various assumed conditions), ninety-two pages are devoted to their detection and measurements. All this is dealt with before the main subject of telegraphy is introduced; this constitutes nearly half the volume. In the historic part an endeavour has been made to leave no contribution of any importance unmentioned; and, what is more difficult to do, satisfactorily to apportion the credit of each discovery and achievement. Whether the author will have succeeded in satisfying all claimants may be more than doubted; it is certainly more than could be expected. But to the reviewer he appears to have presented an exceedingly complete and fair historical account, which may do much toward quietening the strife (healthy enough in its way) with which the subject is attended.

In a few details suggestions could be made toward an improvement of the exposition. Dr. Fleming will probably see as soon as he is told that the top two paragraphs on p. 349 are not perfect. After giving the general solutions of the equations of wave motion

$$H = f_1(z - ut) + f_2(z + ut), \quad . \quad . \quad . \quad . \quad (9)$$

$$E = f_3(z - ut) + f_4(z + ut), \quad . \quad . \quad . \quad . \quad (10)$$

it should be pointed out that  $f_3$  and  $f_4$  are not independent of  $f_1$  and  $f_2$ . It is incorrect to state that  $H$  and  $E$  remain unchanged if  $z$  and  $t$  be changed to  $z + z'$  and  $t + t'$  where  $z'/t' = u$ . This would be true for the first member on the right hand of each; for the second member  $z'/t'$  would require to be minus  $u$ . In fact, the general solution is not that of a wave travelling with unchanged form though each component of it does so travel, one part in one the other part in the opposite direction. Dr. Fleming's alternative statement beginning "in other words" is therefore also incorrect. Further it is not *obvious* (as stated) from equations (9) and (10) quoted above that the periodic quantities  $E$  and  $H$  are in step or phase with one another. In particular it would be interesting to learn his definition of the phase of a *composite* wave. Some of the statements made become true if, instead of the general solution, a simple harmonic solution be referred to. This may represent either a positive or negative wave, but not both simultaneously.

Again, the diagram on p. 407 may roughly represent the lines of force terminating on an antenna at some stage of the oscillation, but it is scarcely a satisfactory representation of the lines existing before a spark begins. As a typographical error we may indicate that on p. 189 near the top *valuable* should read *variable*.

Faults such as these are so few that the mentioning of them will merely serve to accentuate the high excellence of the treatise as a whole. It is a fine achievement.



XLVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 221.]

January 25th, 1911.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

THE following communication was read:—

‘The Skomer Volcanic Series (Pembrokeshire).’ By Herbert Henry Thomas, M.A., B.Sc., F.G.S.

This series of volcanic rocks is developed in the west of Pembrokeshire, and takes its name from the island of Skomer, where the maximum thickness is exposed. The rocks are traceable on the mainland from near St. Ishmaels on Milford Haven to Wooltack Head, and on the west occupy the islands of Midland, Skomer, and the Smalls. The thickness exposed is some 3000 feet, and the lateral extension some 25 miles. The district described is that portion of the mainland known as the Wooltack peninsula, and the islands on the west. The chief evidence bearing on the age of the series is obtainable from the mainland sections, and indicates that the rocks are of pre-Upper Llandovery age; but, from a consideration of the geology of the neighbouring country, it is probable that their true age is Arenig. The rocks are chiefly subaërial lavafloes of extreme thinness and great lateral extent; they are frequently interstratified with red clays, and are separated into two main groups by a thick mass of sedimentary rocks barren of fossils. There is an almost complete absence of pyroclastic rocks, a fact which points to the eruptions being of the fissure-type.

The lavas form well-defined groups in the field, and range from extremely acid varieties with a silica-percentage of about 80 to others with a percentage of less than 50. The rocks of the series fall into eight chief types, two of which are of necessity new; in order of increasing basicity they are as follows:—soda-rhyolites, soda-trachytes (including olivine- and hypersthene-bearing varieties), keratophyres, skomerites, marloesites, mugarites, olivine-basalts, and olivine-dolerites. The last named are probably intrusive. All these types are described in the paper, and several analyses are tabulated. The first five types may be included in the alkaline class; they are rich in soda, and most of the feldspars belong to albite-oligoclase varieties. The last three types are normal subalkaline rocks, in which the feldspars range from oligoclase to labradorite.

The author does not consider that the Skomer rocks have been albitized to a sufficient degree to mask their original characters, and regards them as a mixture of alkaline rocks of Pantellerian affinities, with a subordinate series of more basic subalkaline rocks, the most basic of which are probably intrusive.

February 22nd.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

The following communication was read:—

‘The Geology of the Districts of Worcester, Robertson, and Ashton (Cape Colony).’ By R. H. Rastall, M.A., F.G.S.

After a brief description of the physiography of the district and the general sequence of the rocks composing it, in which the incompleteness of the stratigraphical record is especially noted, a detailed account is given of the structure and characters of the Malmesbury rocks of Worcester and the region near that town. These are shown to include a lower and an upper sedimentary series, predominantly gritty and slaty respectively, and evidently of great thickness, probably over 20,000 feet. The upper division is pierced by granitic dykes, which have been subsequently crushed and foliated, forming ‘phyllite gneiss.’ Certain bands of limestone are metamorphosed by them to pure white marble. A remarkable isolated mass of igneous rock in Brewels Kloof appears to be intrusive, but the rock is andesitic in character. A thin though conspicuous band of ottrelite-schist has been found in Waai Kloof and in the Hex River Pass. All these rock-types are described in detail. Similar, but somewhat less detailed treatment is accorded to the Malmesbury rocks of Robertson and Ashton, and a petrographical description is given of the large granite intrusion of Wolve Kloof, Robertson.

The distribution and characters of the rocks of the Cape and Karroo Systems are only dealt with, in so far as they throw light on the principal subject of the paper; but a fairly full description is given of the occurrences of Enon Conglomerate, which is shown to occupy a series of isolated basins, arranged along an east-and-west line, and to lie with a strong discordance upon all the older rocks. After a careful examination of the ground, it is concluded that the Enon Conglomerate does not overlap the Worcester-Swellendam Fault, as indicated in the official maps; and that conglomerate does not appear to contain any fragments of the Malmesbury rocks, which cannot therefore have been exposed when it was formed.

After a careful discussion of all the available evidence, it is concluded that the Worcester-Swellendam Fault, which has a maximum throw of probably 10,000 feet, is in great part of post-Cretaceous age, although there are indications of earlier movement along the same line of fracture. From a study of the dominant trend-lines of South-Western Cape Colony it is concluded that the district in question is situated at or near the central line of the syntaxis of two great sets of folds at right angles, which have assumed a fan-shaped arrangement in plan, and that the great fault is a line of fracture and subsidence running transversely across these lines of folding. The folding and the faulting are clearly phases of one general series of events, and the faulting probably resulted from a diminution or even reversal of the pressure which had previously given rise to the folding.

March 22nd.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

The following communication was read:—

‘Some Observations on the Eastern Desert of Egypt, with Considerations bearing upon the Origin of the British Trias.’ By Arthur Wade, B.Sc., F.G.S.

This paper deals chiefly with phenomena observed in the Eastern Desert of Egypt, bordering the Gulf of Suez and that part of the Red Sea which is adjacent to its junction with the Gulf. The mounds of igneous debris which flank the coastal hill-ranges are described, and their origin is discussed and connected with the raised-beach phenomena present in the area. The distances to which fragments of igneous rock derived from these hills have travelled in Egypt are shown.

The shore-sands are next dealt with, and their origin ascribed mainly to the breaking down of local rocks, and not necessarily to the denudation of Nubian Sandstone areas as has been supposed. In the marly beds connected with the recent shore-deposits, tiny dolomite-rhombs, similar to those found by Dr. Cullis in the Keuper Marls, are present. Some effects of wind-blown sand are described, especially the wedging of the sand-grains into cracks produced by other forces of disintegration.

Deposits of rock-salt and gypsum are being laid down at present in the area. The alteration of the calcium carbonate in recent shell-beds to gypsum, with the accompanying destruction of organic remains, is noted; and its significance with regard to the origin of gypsum-beds and the concurrent absence of fossils in some of the older series of strata is pointed out. Analyses of different deposits are given, and the presence of sodium carbonate and epsomite-crystals is proved in the encrustations upon recent fossil shells. The characters of the massive older gypsum- and rock-salt deposits are described, together with the distribution and lithological changes in the beds when traced across the area by means of borings and outcrops. The origin of the gypsum series is shown to be connected with inland salt-lake conditions, and evidence is presented which suggests that these conditions were contemporaneous with the Oligocene continental period in Egypt, and with the formation of the well-known beds of the Fayûm in the Western Desert. A sketch-map showing, for the first time, the geology of the islands situated in the mouth of the Gulf of Suez accompanies the paper.

April 26th.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

The following communication was read:—

‘The Llandovery and Associated Rocks of North-Eastern Montgomeryshire.’ By Arthur Wade, B.Sc., F.G.S.

The area dealt with in this paper is in the neighbourhood of Welshpool. It comprises part of the Severn Valley and the whole of the Vale of Guilsfield. A summary of the work done in the area is first given, and the deficiencies of the present geological map are pointed out.

In the detailed succession now worked out, the Ashgillian and the Valentian are for the first time distinguished, while the distinction between the Wenlock and the Ludlow Beds is brought out by means of graptolite zones. The detailed sequence is as follows:—

SALOPIAN. 1000 feet.	Ludlow ..... Yr Allt Group.		3. Sandy flags and shales, sometimes calcareous.
	Wenlock.	B. Western facies.	2. Hard thick flags with thin shale-bands and septaria.
		A. Eastern facies.	1. Thin muddy shales.
VALENTIAN. 700 feet.	Buttington Group (=Tarannon Shales).		Green and purple barren shales.
	Upper Llandovery.	B. Western facies (Cloddiau Group).	2. Thick calcareous flags and mudstones.
		A. Eastern facies (Cefn Group).	1. Blue shales.
	Lower Llandovery.	Powis Castle Group.	Thick calcareous flags, with <i>Pentamerus</i> Limestone. Red sandstone and conglomerate, with occasional limestone developments.
ASHGILLIAN. 50 feet.	Gwern-y-Brain Beds		Black shivery shales, phosphatic, with a band of black crystalline limestone near the base (= <i>Staurocephalus</i> Limestone?).
CARADOCIAN. 1300 feet.	Gaer-fawr Group.		3. Calcareous mudstones and limestones (= Bala Limestone); coarse, ashy, felspathic bands.
			Thin, phosphatic, pale-grey shales at the base.
	Pwll-y-Glo Group.		2. Massive grits, with bastard limestones. 1. Flags and grits, with some shale-bands.
GLENKILN-HARTFELL (= <i>Dicranograptus</i> Shales).	Trilobite Dingle Group.		Shales and flags, with some grit-bands.
			2. Nodular mudstones and grey shales, with <i>Trinucleus</i> . 1. Splintery grey shales, with <i>Diplograptus</i> ( <i>Mesograptus</i> ) <i>fcliazeus</i> , etc.

The stratigraphical succession is shown by traverses; but, owing to successive overlap of the upper beds, no single traverse gives the full succession. The different groups are traced over the area mapped, and the chief fossiliferous exposures described, with full lists of the fossils obtained. The district is shown to be transitional in character between neighbouring districts on almost every side, combining many of their features.

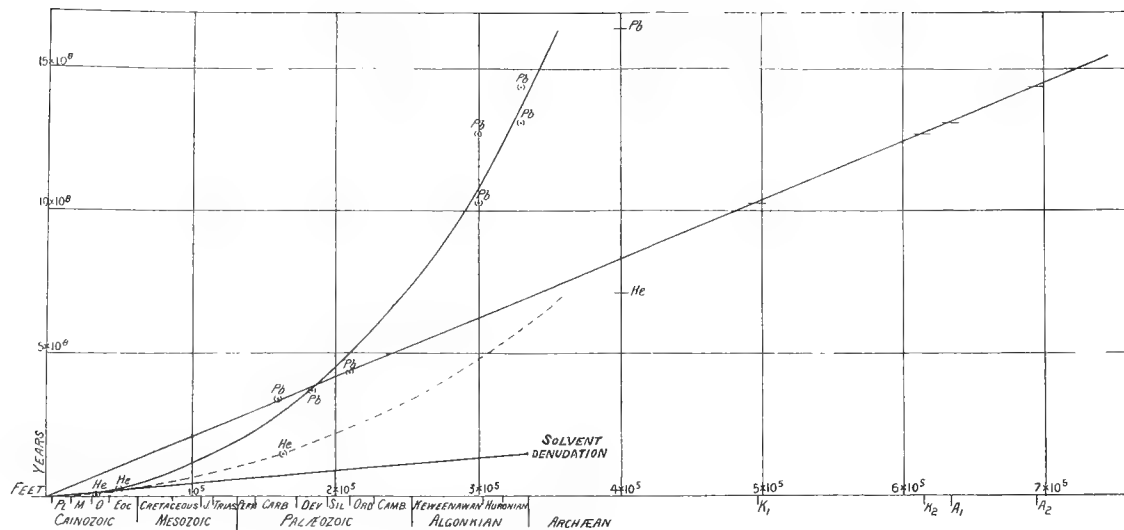
The structure of the area is mainly that of an anticline with 'keystone' faulting, the dominant features being determined by the intrusive masses of the Breidden Hills and the small Standard Dyke of Welshpool. The two boundary-faults of the arch have very considerable downthrows.

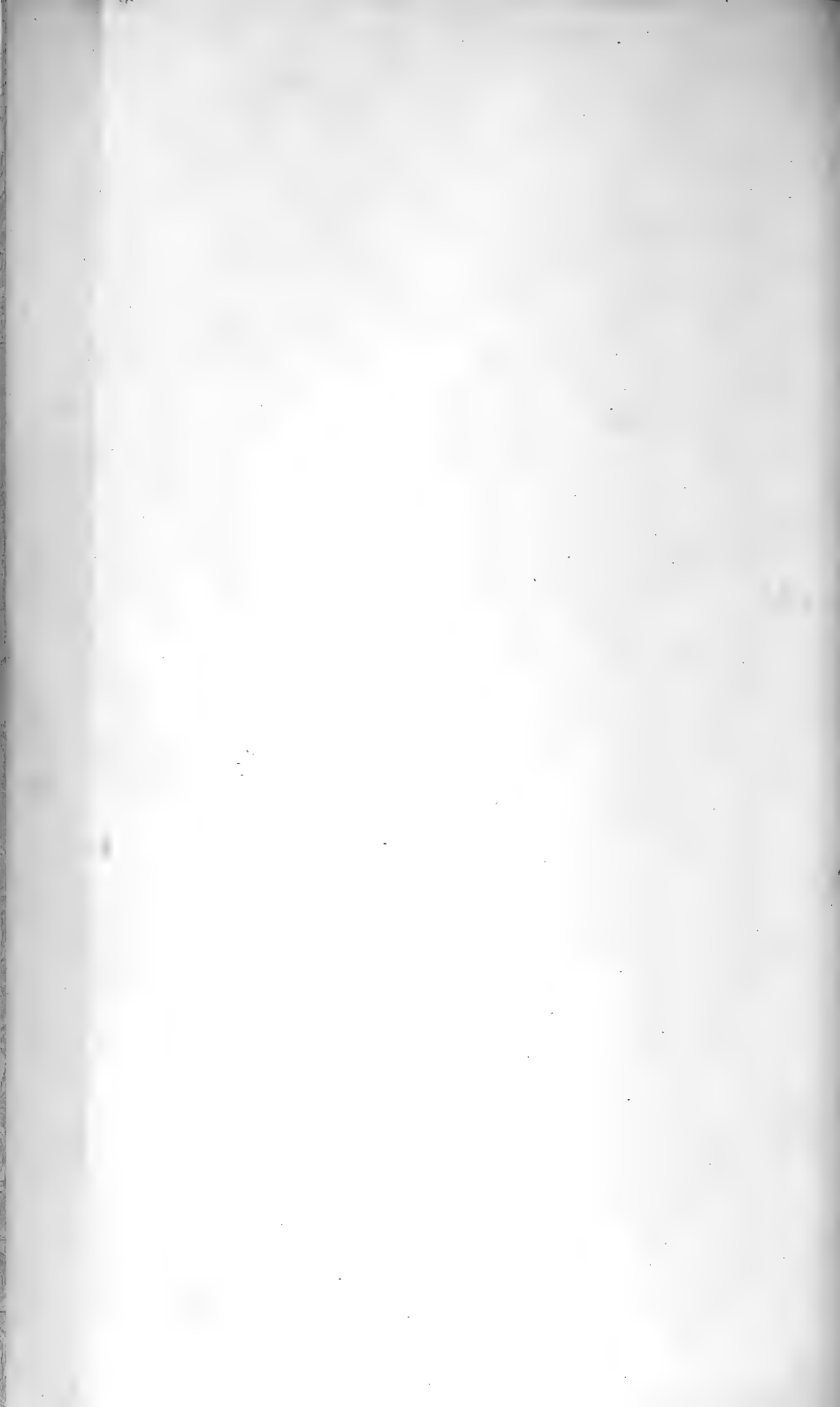
A brief account is given of the Welshpool Dyke, with chemical analyses of the rocks.

The Glacial geology of the area is also described, three series of deposits being observed: (1) a high-level series, (2) a low-level series, and (3) a stratified series. The Guilsfield Valley is shown to have been occupied by a Glacial lake, and the reversed drainage of the Cefn-Yspn Brook is shown to be connected with a 'col' through which the overflow water drained.











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OCTOBER 1911.

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XLVII. *The Resonance Spectra of Iodine Vapour and their Destruction by Gases of the Helium Group.* By R. W. WOOD, Professor of Experimental Physics, Johns Hopkins University, Adams Research Fellow of Columbia University\*.

[Plates IV. & V.]

SHORTLY after the discovery of the resonance spectrum of iodine vapour *in vacuo* excited by the radiations from a mercury vapour lamp, the remarkable effect of the presence of small traces of helium in transforming the sharply defined resonance spectrum into the complete band spectrum, such as is excited by white light, was described by the author and J. Franck (Phil. Mag. Feb. 1911). It was shown that the band spectrum appeared as a faint background when the helium was at a pressure of less than one millimetre, while a pressure of between 5 and 10 mm. destroyed the resonance spectrum entirely, its place being taken by the band spectrum. The total amount of light radiated in the two cases was about the same, the helium appearing to act as an agent in transferring the energy from the excited system of electrons to all of the other systems, which remained quiescent when the iodine vapour was *in vacuo*.

In the present paper I propose to take up the further study of the resonance spectra, and the effect of the other gases of the helium group, as well as the remarkable polarization

\* Communicated by the Author.

Phil. Mag. S. 6. Vol. 22. No. 130. Oct. 1911. 2 I

of the light emitted by the vapour when stimulated by monochromatic radiations and white light.

A number of improvements have been made in the arrangement of the apparatus, and it is now possible to show the resonance spectrum to a class in optics by means of a commercial Cooper-Hewitt lamp (in glass) and a small pocket spectroscope. A glass tube 2 or 3 cm. in diameter and 30 cm. long is used. One end is blown out into a small bulb of a diameter only slightly larger than that of the tube, care being taken to get the glass as free from striæ as possible. It is especially important to get rid of the small drop of glass which usually forms at the point where the tube is drawn down. The tube is now carefully dried, and after the introduction of a few small crystals of iodine, drawn down to a thick-walled capillary at the other end, highly exhausted with a mercury pump, and sealed. It is then mounted alongside of, and almost in contact with, the Cooper-Hewitt lamp, the direct radiation unconcentrated by lenses being used. On looking down the axis of the tube through the bulb the yellowish fluorescent light is seen, and the spectroscope exhibits the discontinuous resonance spectrum composed of isolated bright lines. If the light from the carbon arc, or still better sunlight, is concentrated at the centre of the tube as near the bulb as possible, the characteristic band spectrum excited by white light appears. The ease with which this experiment can be performed makes it of interest in view of the importance of resonance and band spectra in connexion with the theory of the radiation of electrons.

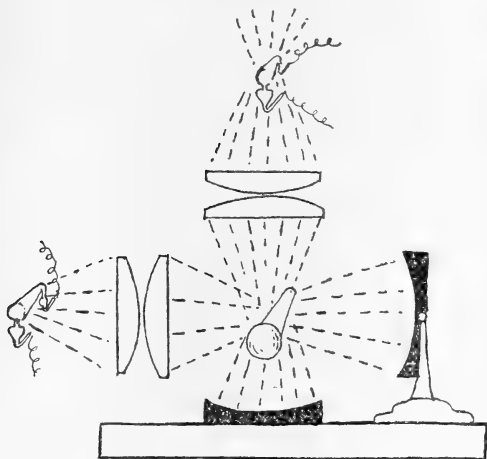
If helium is available, a second tube may be prepared for showing the transformation of the resonance into the band spectrum. The tube is prepared as before, and the gas introduced until the manometer indicates a pressure of about 5 mm., after which it is sealed off from the pump. These tubes keep indefinitely, require no heating, and may be set up for exhibition in two or three minutes. The only advantage of the quartz mercury arcs used in the present investigation lies in the greater intrinsic brilliancy of the light.

The use of glass bulbs for the study of the fluorescence has been discontinued, as it has been found that tubes similar to those described above give greater brilliancy and far less trouble resulting from reflexion of the light of the arc from the walls. It will be found advantageous to wrap the end of the tube with black cloth; this gives us a dark background against which the fluorescent light stands out.

The present investigation was made in the laboratory of the Royal Institution, which was placed at my disposal through the courtesy of Sir James Dewar, the investigation of many points being made possible by the giant Nicol prisms, condensing-lenses, and other apparatus not usually found in physical laboratories. I am also under great obligation to Mr. Twyman, of the firm Adam Hilger & Son, who placed echelons, spectrographs, and other optical apparatus at my disposal, and to Mr. Kenneth Mees, who very kindly lent me his small prism spectrograph, with which most of the photographs illustrating this paper were made.

Thanks to improvements made in the method of illuminating the vapour, it was possible to obtain the resonance spectrum with sufficient brilliancy to permit of its examination with the echelon, which is of great importance in connexion with the proposed examination for a possible Zeeman effect. I searched for the effect in the laboratory of M. Cotton in Paris with a large Weiss electromagnet, but at that time it was impossible to obtain the spectrum with a brilliancy sufficient to permit of its examination with any spectroscope of high resolving power, and nothing was accomplished.

Fig. 1.



The arrangement of the apparatus built up at the Royal Institution is shown in fig. 1. Two large quartz mercury arc-lamps made by the Westinghouse Cooper-Hewitt Co., of London, which I have found to be much more powerful than any lamps which I have used previously, were used for

illuminating the vapour. One of these was mounted above the tube, and the rays, after having been brought to a focus at the centre of the tube by a condensing lens of 25 cm. aperture, were returned to the same focus by means of a large concave mirror placed below the tube (which was at the centre of curvature of the mirror). One lamp was thus made to do the work of two. The other lamp was mounted to one side of the tube with a similar arrangement of lens and mirror. The mercury arc-lamps were about 12 cm. in length, and their images formed along the axis of the iodine tube by the condensing lenses and mirrors were of the same dimensions.

This arrangement appears to give us very nearly the maximum amount of illumination possible, the only improvement which I have been able to think of being an iodine tube completely surrounded by a mercury arc burning in a long closely-wound spiral tube of quartz. I have also had constructed a glass mercury arc with the iodine tube passing axially down its centre, but I have not yet succeeded in getting it to work very well. With the arrangement just described, I found that I could get a fully exposed photograph of the resonance spectrum with a Hilger wave-length spectrograph in less than two hours, whereas in the earlier experiments exposures varying from 18 to 24 hours were necessary. The greatly increased brilliancy of the fluorescence which is obtained by the use of a tube can be ascribed to the following circumstance. It was found that when a large bulb was used, as in the earlier experiments, if the light was returned to the focus by a concave mirror placed behind the bulb, the cone of fluorescent light produced by this reflected beam was so faint that it contributed very little to the total intensity. This resulted from the absorption of the exciting frequencies by the iodine vapour. It is obvious that if we employ a bulb and focus the light at its centre, much of the available energy is lost before the rays come to a focus. This difficulty is avoided by the use of a tube, since the exciting rays traverse only the small volume of iodine vapour which is under observation.

The green line and both of the yellow lines of the mercury arc are capable of exciting resonance spectra which can be exhibited separately. If we interpose a glass cell containing a strong solution of eosine between the arc and the iodine tube, the resonance spectrum excited by the two yellow lines appears: this consists of a beautiful series of equidistant doublets, fifteen in all (30 lines), two below and twelve above the yellow exciting lines. The series of equidistant lines

excited by the 5790 mercury line is much more intense than the series excited by the 5770 line, a circumstance which we may safely ascribe to a closer coincidence between the wavelength of the less refrangible yellow line of mercury and one of the absorption-lines of the iodine vapour.

The yellow light can be removed from the exciting radiations by means of a saturated solution of neodymium chloride, and we obtain in this case the series excited by the green mercury line.

Photographs of the spectra obtained in this way are reproduced on Pl. IV. Fig. 1 is the composite of the three resonance spectra excited by the total radiation of the mercury arc, the green and the two yellow exciting lines being indicated by arrows. The short-line spectrum which runs along the centre is the neon spectrum, which, being very rich in orange and red lines, was used for a comparison spectrum in the present investigation. Fig. 2 shows the same spectrum without the neon lines. The broadening of the lines is due to overexposure, the fainter lines appearing sharp. The series excited by the green mercury line operating alone is shown in fig. 3. This is one of the finest cases of a resonance spectrum made up of equidistant lines that I have found up to the present time, eighteen members having been photographed and measured. The gradual decrease in the distance between the members of the series as the red end of the spectrum is approached, is of course due to the circumstance that the photograph was made with a prism spectrograph. As a matter of fact the interval between the lines increases slightly with an increase of wavelength. The more or less regular alternation between very strong lines and very weak lines, which is characteristic of so many of the resonance spectra of sodium vapour, is very conspicuous; in fact, this spectrum reminds one forcibly of the resonance spectrum of sodium excited by the cadmium line 4800, in which case we have the exciting line followed by a strong line, then a faint line, then four strong lines, a faint line, and four more strong lines. In the case of iodine we have the exciting line followed by a strong line, then a faint line, a strong line and a faint one, two strong lines, a faint line, strong, faint, strong, two faint lines, strong, faint, strong.

Fig. 4 is a photograph of the resonance spectra excited by the two yellow lines of mercury, the green line having been removed by the eosine screen. We find here 15 pairs of lines, reminding us of the repetition of the magnesium triplet in the case of the resonance spectrum of sodium

vapour. In the earlier work upon iodine it was thought that the series excited by the longer of the two yellow lines coincided with the series excited by the green line. The higher dispersion used in the present work shows that this is not the case, for although coincidence is so nearly approached in the vicinity of the yellow lines that only the sharpest photographs taken with such a fine slit that their reproduction is impossible, show separation, the larger value of the spacing in the case of the series excited by the yellow line 5790 causes the lines of this series to get so far out-of-step with the lines of the series excited by the green mercury line, that the failure of coincidence is clearly visible in the photographs reproduced, in the red region of the spectrum. (Compare figs. 3 and 4.)

The transformation of the resonance into the band spectrum is shown in the photograph reproduced in fig. 5, with the neon spectrum superposed. The darker portion of the spectrogram has been intensified with mercury bichloride, to bring out the bands more distinctly. This photograph was taken with a large glass bulb containing helium at 5 mm. in addition to the iodine. The behaviour of the other gases of the helium group has been investigated in this respect and will be discussed presently.

The wave-lengths of the lines in the various series have been determined with great care, from a large number of photographs. Short exposures were made with a very fine slit for the strong lines, since the long exposures which were necessary to bring out the faint lines resulted in so much broadening of the stronger lines that their exact measurement was impossible.

The wave-lengths of the lines are given in the following Table. In column A we have the series excited by the green line 546, in column B the series excited by the yellow line 5769.5, and in column C that resulting from the yellow line 5790.5. The exciting lines are printed in heavy type. In columns *a*, *b*, and *c* we find the wave-length differences of the lines of the corresponding series. Column *d* gives the wave-length differences between the members of the 15 pairs of lines excited by the two yellow lines (the B and C series).

As appears from the table the wave-length differences have a tendency to become larger as we approach the red end of each of the series. There is also a certain amount of oscillation, that is, the differences do not increase steadily and uniformly. I am of the opinion that the wave-lengths can be considered correct in most cases to an Ångström unit

TABLE.

A.	B.	C.	a.	b.	c.	d.	e.
6726	6810	6850					
.....	.....	.....					
.....	6625	6660	$84 = \frac{168}{2}$	85	90	40	74.4
6558	6546	6578	$\frac{163}{2}$	79	82	35	
.....	6460	6490	$81.5 = \frac{163}{2}$	86	88	32	73
6395	6373	6402	82	87	88	30	
6313	6296	6323	77.5	77	79	29	71.8
6235.5	6217.5	6240	76	78.5	83	27	71
6159.5	6140	6161	75	77.5	79	22.5	70.4
6084.5	6063.5	6084.5	73.5	76.5	76.5	21	69.8
6009.5	5985	6009.5	72	77.5	75	21	69.3
5936	5910	5936	72	75	73.5	24.5	68.5
5864	5840.5	5864	68.5	69.5	72	26	67.8
5792	<b>5769.5</b>	<b>5790.5</b>	63.5	71	73.5	23.5	67.1
5723.5	5698	5723.5	68.5	71.5	67	21	66.2
5657	5630	5658.5	64	68	65	25.5	65.6
5588.5			63.5			28.5	65.3
5524.5			64.4				63.7
<b>5461</b>			59.1				63.5
5396.6							64.4
5337.5							62

or perhaps a little less, but as I have pointed out in a previous paper, the measured wave-length of a line may be slightly in error resulting from absorption, *i. e.* one side of the emission-line may be removed by a neighbouring absorption-line, its centre of gravity appearing shifted. This may perhaps be the cause of the irregularities observed. If the spacing were accurately constant the wave-lengths of the lines of the series could be represented by the following formula:  $\lambda = \lambda_0 \pm mk$ , in which  $\lambda_0$  is the wave-length of the exciting line,  $m$  is a natural number, 1, 2, 3, etc., and  $k$  is the common difference. The value of  $k$  is obtained by taking the difference between the wave-length of the exciting line and that of any other line and dividing it by that particular value of  $m$  which fixes the position of the line in question in the series. This arrangement was adopted in a previous paper treating of the resonance spectra of sodium by Wood and Hackett (*Astro-Phys. Journ.* vol. xxx. No. 5, 1909), since it prevents the double discrepancy which arises when the other arrangement is used. The values of  $k$  obtained in this way for the series excited by the green mercury line are given in column *e*, which should be compared with column *a*.

In the case of sodium vapour this increase in the value of  $k$  with increasing wave-length was observed in many cases, though the increment was not as marked as in the case of iodine.

*Transformation of Resonance Spectra by Gases of the Helium Group.*

The introduction of helium into the iodine vacuum-bulb results, as has been pointed out, in the development of the band spectrum which we have when we excite the vapour with white light.

A photograph of the band spectrum, with the resonance lines superposed, excited by the light of the mercury arc when the iodine vapour is mixed with helium at 5 mm. pressure, is reproduced on Pl. IV. fig. 5. The band spectrum appears faintly when the helium is at a pressure of a millimetre or less, and as the helium pressure increases, the intensity of the band spectrum increases, while that of the resonance spectrum decreases, the total amount of emitted light remaining about the same, however. It is still an open question whether both spectra are emitted simultaneously by the same molecule. I am rather doubtful about this, for it seems more probable that when the helium is at a very low pressure, the band spectrum is emitted only by those molecules which at the moment happen to be within the sphere of influence of a helium molecule. It is possible that a momentary combination between a helium atom and one of iodine may exist either normally or under the action of light. Sir J. J. Thomson has found that such momentary combinations exist between atoms in vacuum-tubes developing canal rays, which would be considered impossible by the chemists. It would be extremely interesting to investigate the positive rays excited in a mixture of helium and iodine by Thomson's very beautiful method.

It appeared to be of the greatest importance to investigate the behaviour of the other gases of the helium group in this respect, for, as has been shown in a previous investigation by Wood and Franck, the commoner gases, hydrogen, nitrogen, oxygen, etc., are wholly without influence in developing the band spectrum. Thanks to the kindness and interest of Sir William Ramsay and Professor Collie, the gases argon, neon, krypton, and xenon were placed at my disposal.

We will consider the behaviour of the gases in the order of their molecular weight.

In helium, with a molecular weight of 4, at a pressure of 10 mm., the band spectrum is very strong and there is scarcely a trace of the resonance spectrum. In neon at the same pressure (weight 20) the resonance spectrum is relatively much stronger. This is partially in accord with the views expressed in a previous paper by Franck and Wood,



regarding the relation between the affinity of a gas for electrons and its action in destroying fluorescence. According to the investigations of Franck neon has the smallest electron affinity of all the gases, less even than that of helium. According to our theory, if a gas has a strong affinity for electrons it destroys completely the emission of all of the fluorescing molecules which at the moment happen to be within the sphere of action of one of the gas molecules, without, however, affecting the nature of the radiation of the iodine molecules which at the moment happen to be outside of the sphere of action. This means that as the pressure of the gas is increased, more and more of the iodine molecules are within the sphere of action at any given moment and fewer and fewer of them emit light; the resonance spectrum therefore gradually fades away without any trace of the band spectrum appearing. In the case of a gas having small affinity for electrons, we find that we can have it present at a relatively high pressure without any great reduction in the total amount of light emitted by the iodine, and that it operates in some manner, the nature of which we cannot at present surmise, in transferring the energy from the excited system of electrons to all of the other systems present in the molecule. The question now arises as to whether the efficiency of these gases in developing the band spectrum depends upon their molecular weight, or upon some other property. Neon is five times as heavy as helium, yet at the same pressure (10 mm.) the resonance spectrum is relatively much stronger.

We cannot be quite sure of the exact relations until photometric measurements have been made of the intensity of the resonance spectrum and the band spectrum of iodine in the gases of the helium group at different pressures. In argon, at 6 mm. pressure the total light emitted is much less than in neon and helium at 10 mm., but the resonance spectrum is stronger in proportion to the band spectrum than in the case of neon at 10 mm. In krypton (weight 83), at 1.7 mm. pressure the intensity of the emitted light is reduced to about  $\frac{1}{2}$  of its original value and the spectroscope shows only the barest trace of the band spectrum, practically all of the light remaining localized in the resonance lines, as is the case with the common gases. In xenon (weight 130), at 1.5 mm. pressure the intensity is found reduced to about  $\frac{1}{4}$  of its original value with no trace whatever of the band spectrum. Helium, the lightest of these rare gases, thus appears to be the most efficient in developing the band spectrum. I had expected to find neon more efficient than

helium, for it has a smaller affinity for electrons according to Franck, and exhibits most remarkable electrical properties. Professor Collie showed me a tube about half a metre long containing neon at a pressure of an atmosphere and a half, through which the discharge of an induction-coil passed in preference to an alternative spark-gap in air of less than a centimetre arranged in multiple with the tube. In neon, however, the intensity of the emitted light is about the same as in helium at the same pressure, and much more, it is localized in the resonance lines.

This matter requires a more careful investigation, for I was able to devote not more than the two or three days immediately preceding my departure from London to this part of the investigation.

### *Polarization of the Light in Resonance Spectra.*

The polarization of the light of fluorescent gases was discovered by the author more than three years ago (Phil. Mag. July 1908). It was found to be much stronger in sodium and potassium than in iodine vapour. This subject has been taken up again, in view of its great importance in connexion with the genesis of resonance spectra, and I now find that it is possible to obtain almost as strong polarization with iodine vapour as was formerly observed with sodium. This is probably due to the fact that in the earlier work very small glass bulbs were used, which quite possibly were insufficiently exhausted. In the case of the resonance spectra I never felt quite satisfied with my observations, though I obtained what I considered fair evidence that when the fluorescence was excited by polarized monochromatic light, the light was polarized in all of the lines of the resonance spectrum. This has been fully corroborated in the present work, by a method which admits of no doubt.

The percentage of polarization was first determined in the case of iodine vapour excited by polarized white light, by the same method used in the earlier investigation.

It was found that the Savart fringes could be destroyed by two glass plates at an angle of  $43^\circ$ , and by one glass plate at an angle of  $56^\circ$ , and the percentage of polarization comes out as 17 in each case. For sodium vapour I found 20 per cent. of polarization, or in the case of very rare vapour at a low temperature, as high as 30 per cent.

The polarization was easily observed when the fluorescence was excited by the mercury arc, the large glass bulb, 20 cm. in diameter, used for the demonstration of the fluorescence before a large audience, being found best adapted to the

work. The light from the arc was first rendered parallel by means of a large condenser, then passed through a Nicol prism of about 13 cm. aperture, and finally focussed at the centre of the bulb by a second condenser. A large Savart plate was mounted to one side of the bulb, and the fringes viewed through a second large nicol. It was first necessary to get rid of all reflexions of polarized light from the walls of the bulb and room. This was accomplished by means of screens suitably placed, and a background of black velvet. To make sure that the fringes resulted wholly from the fluorescent iodine vapour, the wall of the bulb was touched with a bit of cotton soaked with liquid air. This immediately condensed the vapour, destroyed the fluorescence and all trace of the fringes, the background appearing perfectly black. It is of course necessary to get the bulb in such a position that none of the internal reflexions comes from the region where the fringes are observed.

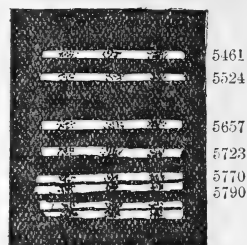
On Pl. V. fig. 1 we have a photograph of the fluorescence of the vapour excited by the mercury arc without the nicols or Savart plate, and (fig. 2) a photograph of the Savart fringes crossing the cone of fluorescent light. It was thought that possibly the percentage of polarization could be increased by reducing the density of the iodine vapour. The oblique plates by which the polarization was compensated were set at such an angle as to just cause the disappearance of the fringes, under which condition any increment in the percentage of polarization would cause their reappearance.

The outside of the bulb was now touched with cotton soaked with liquid air, which caused a rapid condensation of the iodine vapour. The cone of fluorescent light faded gradually away, but the Savart fringes did not reappear, though the results obtained with sodium vapour made me think that at the lowest vapour densities consistent with visible fluorescence, increased polarization might be expected. Warming the bulb to increase the vapour density above the value which it has at room temperature did not appear to decrease the amount of polarization, though the intensity of the fluorescence was considerably diminished.

The investigation of the polarization of the resonance lines was next investigated. This I regard as one of the most important points in the whole investigation, for if the bright lines excited by polarized monochromatic light are themselves polarized, it indicates that the directed motion passed over by the light-waves to the resonant electron is passed on as directed motion to the other electrons, or whatever the centres of emission of the bright lines of the resonance spectrum

may be. The Savart fringes were formed as before, cutting vertically across the horizontal cone of fluorescent light excited by the polarized light from the mercury arc. A screen of black paper, perforated at its centre with a horizontal aperture about 3 cm. in length by 2 mm. in width, was now mounted between the bulb and the Savart plate in such a position that the aperture covered the brightest part of the fluorescent cone. On looking through the analysing nicol the aperture was seen brightly illuminated except for the dark regions where it covered the Savart fringes. A direct-vision prism of high dispersion was now held before the eye, oriented in such a way as to give vertical dispersion. A vertical spectrum, or a series of images of the aperture corresponding to the brightest lines of the resonance spectrum was clearly seen, and the fringes cut across all of these images (fig. 2) and were quite as distinct in the images corresponding to wave-lengths not present in the mercury arc as in those due to light which was re-emitted from the vapour without change of wave-length (resonance radiation). This method was far more satisfactory than the one employed for the same purpose in the case of sodium vapour, and gave results about which there could be no question. The addition of helium appears to diminish the percentage of polarization, for in the bulb containing helium at a pressure of 10 mm., the percentage of polarization was found to be only 13, against 17 when the iodine vapour was *in vacuo*. In helium at 10 mm. the resonance spectrum is completely replaced by the band spectrum, and the fact that polarization is still present indicates that the polarized vibration is passed over to the other electron systems.

Fig. 2.



#### *Resonance Spectra with the Echelon.*

Through the courtesy of Mr. Twyman, who placed a number of very fine echelons made by the Hilger Company at my disposal, I was able to make a preliminary study of the appearance of resonance spectra under high resolving power. The first inspection was very discouraging, for the width of the lines turned out to be as great as, or greater than, the distance between the orders.

It was at once observed, however, that this same condition existed in the case of the exciting radiations from the mercury arc, on account of the great density of the mercury vapour in the red-hot quartz tube. The mercury lamp was accordingly extinguished and allowed to cool off. On relighting the lamp, the fluorescence of the iodine vapour was at first too feeble to permit of observation with the echelon, but as it gradually brightened, as the temperature and intensity of the mercury lamp increased, the lines appeared, and were observed distinctly narrower than the distance between the orders. Moreover, their width appeared to be the same as that of the exciting lines of the arc, which came out much stronger than the resonance lines on account of diffused light. As the arc lines widened, the resonance lines increased in width at the same rate, until they fused into a continuous band, due to the overlapping of orders. Calculation showed that the width of the lines when they were first observable in the echelon was of the order of  $1/20$ th of the distance between the D lines. It seems probable that, by still further improving the conditions, a more extended study of resonance spectra with the echelon can be made. To do this it will be necessary to excite the fluorescence by a low temperature mercury arc burning in glass. Probably a long iodine tube passing along the axis of a Cooper-Hewitt lamp, so as to be completely enveloped by the arc except at the ends, would give the desired results.

I have succeeded in obtaining resonance spectra from iodine vapour with other monochromatic excitations, but have not yet studied them.

XLVIII. *On the Rigidity of the Earth.* By J. PRESCOTT, M.A., Lecturer in Mathematics at the Manchester School of Technology\*.

THE interest in the question of the rigidity of the earth has been revived in recent years by the careful and convincing experiments of Dr. Hecker of the Prussian Geodetic Institute†. Dr. Hecker placed two horizontal pendulums at right angles to each other and introduced devices for recording the motion of the pendulums for a long period of time. The motions of the two pendulums are the same as the component motions of the bob of a

\* Communicated by the Author.

† *Beobachtungen an Horizontalpendeln, des k. Preussischen Geodätischen, Instituts.* Neue Folge, N. 32 (1907).

simple pendulum of great length. The motion actually recorded is the motion which the bob of this simple pendulum would have relative to the solid earth in the neighbourhood of the point of observation; for, of course, the recording apparatus moves with the solid earth to which it is attached. The motion of the pendulum-bob is due to several causes of which two are the attractions of the sun and moon; that is, the tidal actions of these bodies. If the earth yielded to these attractions as freely as a liquid earth then no relative motion of the pendulum and the solid earth would be observed because the plumb-line would always be perpendicular to the surface. But if the solid earth were perfectly rigid the plumb-line would change its direction slightly with the positions of the sun and moon, and the plan of the bob would trace out a certain curve on the surface of the earth, which curve can be calculated from the known actions of the sun and moon. It is obvious then that the observed relative motion gives us the necessary data for calculating the extent to which the earth yields to tidal actions; and thence we can deduce a value for the rigidity of the earth. It is the object of the present paper to make the necessary calculations on the yielding of elastic spheres for the purpose of comparison with observations and to find therefrom the average rigidity of the earth.

So far as I know all previous calculations have been made for spheres of uniform density. Now we know that the density of the earth is by no means uniform throughout, and it seemed very likely beforehand that a sphere of variable density might yield to a very different extent from a sphere of uniform density. In this paper I have assumed laws of density which agree pretty well with what we know concerning the earth's density. Taking the density of water as  $w$  I have made the mean density  $5.5 w$  and the density at the surface  $2.5 w$ .

The analysis is difficult and I have only succeeded in solving the problem by assuming the sphere to be incompressible. But there would be little advantage in any other assumption because we can infer from the corresponding calculations for spheres of uniform density that the degree of compressibility has little effect on the deformation. The ellipticities calculated with the two different assumptions that the earth is incompressible and that Poisson's ratio is  $\frac{1}{4}$ , differ only by about one per cent. The results are compared in Love's *Elasticity*, Art. 183. If Poisson's ratio is put equal to  $\frac{1}{4}$  in my own result, given in *Phil. Mag. Sept.*

1910, it will be found that this also gives about the same difference from the result for an incompressible sphere.

In the following calculations I assume that if the tidal force did not act the density of the sphere at distance  $r$  from the centre would be a function of  $r$  only. When the tidal force acts it is assumed that each naturally spherical shell is deformed into a spheroid of small ellipticity  $e$ , which is a function of  $r$ . The additional assumption of incompressibility enables me to express the strains in terms of  $e$ ,  $r$ , and differential coefficients of  $e$  with respect to  $r$ . Then there are two equations of equilibrium of an element of the material, either of which, it might appear, ought to give a differential equation for  $e$ . But since the cubical dilatation has been assumed zero and the bulk-modulus infinite, the product of these two quantities, which appears in each of the equations of equilibrium, is an unknown quantity and has to be eliminated from the equations. The eliminant is the differential equation for  $e$ .

In the differential equation for  $e$  the variation of the density with  $r$  is involved and it becomes necessary to assume an expression for the density. If  $\rho$  is the density,  $a$  the external radius of the earth, I have used two expressions for the density, viz,

$$\rho = \left(10 - 7.5 \frac{r^2}{a^2}\right)w, \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$\text{and} \quad \rho = \left(14.5 - 12 \frac{r}{a}\right)w, \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

where  $w$  is the density of water.

It will be found that both these densities give a mean of  $5.5 w$  at the surface where  $r=a$ .

Taking the modulus of rigidity to be  $800 \times 10^6$  grams per square centimetre, about the value for wrought iron, I find that the ellipticities of the surface are proportional to 0.325 and 0.321 corresponding to the densities (a) and (β) respectively. Then using the density (a) I recalculate the ellipticity taking the rigidity to be half that of wrought iron, that is,  $400 \times 10^6$  grams per square centimetre, and I find in this case that the ellipticity is represented by 0.473. These results are afterwards used to calculate the quantity measured by Dr. Hecker's pendulums.

The ellipticities calculated on the assumption of uniform density corresponding to the two moduli of rigidity mentioned above are represented by the numbers 0.394 and 0.600. When these are compared with the ellipticities for variable





The above is most easily seen by considering that  $\eta$  is the rotation of the radius vector  $r$ , and

$$\frac{1}{2} \left\{ r \frac{\partial \eta}{\partial r} - \frac{1}{r} \frac{\partial \epsilon}{\partial \theta} \right\}$$

is the rotation relative to the radius vector.

The two rotations in planes perpendicular to the plane of  $\omega$  are clearly zero.

All the conditions of equilibrium are satisfied by assuming that a shell of uniform density which is spherical in the unstrained state will be strained into a spheroidal shell. This will be evident in the course of the subsequent work.

On account of the difficulties of the analysis I am assuming that the sphere is incompressible.

Since  $r$  denotes the unstrained distance of an element from the centre of the sphere both the preceding assumptions are involved in the equation

$$\epsilon = re(\cos^2 \theta - \frac{1}{3}). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Both the ellipticity  $e$  and the density  $\rho$  must be regarded as functions of  $r$ . We may regard  $r$  itself as the parameter of a shell of uniform density.

The assumption of incompressibility gives also the equation

$$0 = \delta = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \epsilon) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\eta \sin \theta). \quad . \quad . \quad . \quad (7)$$

Equations (6) and (7) enable us to express  $\eta$  in terms of  $e$ . Thus, using equation (6),

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \epsilon) = \left( \cos^2 \theta - \frac{1}{3} \right) \frac{1}{r^2} \frac{d}{dr} (r^3 e). \quad . \quad . \quad . \quad . \quad (8)$$

Equations (7) and (8) now give

$$\begin{aligned} \eta \sin \theta &= -\frac{1}{r^2} \frac{d}{dr} (r^3 e) \int \left( \cos^2 \theta - \frac{1}{3} \right) \sin \theta d\theta + f(r) \\ &= \frac{1}{r^2} \frac{d}{dr} (r^3 e) \left\{ \frac{1}{3} \cos^3 \theta - \frac{1}{3} \cos \theta \right\} + f(r) \\ &= -\frac{1}{3r^2} \cos \theta \sin^2 \theta \frac{d}{dr} (r^3 e) + f(r), \quad . \quad (9) \end{aligned}$$

where  $f(r)$  is an arbitrary function of  $r$  which arises from integrating with respect to  $\theta$ . But since  $\eta$  is zero when  $\theta$  is zero it follows that  $f(r)$  is also zero.

Now by equations (5), (6), and (9)

$$\begin{aligned} 2r\omega &= \frac{\partial}{\partial r}(r^2\eta) - \frac{\partial \epsilon}{\partial \theta} \\ &= -\frac{1}{3}\cos\theta\sin\theta\frac{d^2}{dr^2}(r^3e) + 2re\cos\theta\sin\theta. \quad (10) \end{aligned}$$

Let  $k$  be the bulk-modulus and  $n$  the rigidity-modulus of the sphere. These are assumed to be constant throughout since average values are all we can hope for from theoretical investigations.

The equations of equilibrium in the present case, where everything is symmetrical about the axis from which  $\theta$  is measured, are (see Love's 'Theory of Elasticity,' Art. 125),

$$\left(k + \frac{4}{3}n\right)\frac{\partial \delta}{\partial r} - \frac{2n}{r\sin\theta}\frac{\partial}{\partial \theta}(\omega\sin\theta) - \rho\frac{\partial W}{\partial r} = 0, \quad (11)$$

$$\left(k + \frac{4}{3}n\right)\frac{\partial \delta}{\partial \theta} + 2n\frac{\partial}{\partial r}(r\omega) - \rho r\frac{\partial W}{r\partial \theta} = 0, \quad (12)$$

where  $W$  is the potential of the external forces on the element whose coordinates in the unstrained state are  $r$ ,  $\theta$ , and  $\rho$  is the density of the element.

Now the assumption of incompressibility makes  $\delta$  zero and  $k$  infinite, but it leaves  $k\delta$  finite, since this is the negative of hydrostatic pressure. The best thing to do is to eliminate  $k\delta$  from (11) and (12).

Differentiating (11) with respect to  $\theta$  and (12) with respect to  $r$  and then subtracting corresponding sides of the resulting equations we get

$$\begin{aligned} \frac{2n}{r}\frac{\partial}{\partial \theta}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}(\omega\sin\theta)\right\} + 2n\frac{\partial^2}{\partial r^2}(r\omega) \\ - \frac{\partial}{\partial r}\left(\rho\frac{\partial W}{\partial \theta}\right) + \frac{\partial}{\partial \theta}\left(\rho\frac{\partial W}{\partial r}\right) = 0. \end{aligned}$$

Now making use of the fact that  $\rho$  is a function of  $r$  and not of  $\theta$  we can write this last equation in the form

$$\begin{aligned} \frac{n}{r^2}\frac{\partial}{\partial \theta}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}(2r\omega\sin\theta)\right\} + n\frac{\partial^2}{\partial r^2}(2r\omega) - \frac{\partial W}{\partial \theta}\frac{d\rho}{dr} = 0. \\ \dots\dots\dots (13) \end{aligned}$$

When we have substituted for  $2r\omega$  and  $W$  in this equation we shall have the differential equation from which  $e$  is to be found.

From equation (10) we get

$$\frac{\partial}{\partial \theta}(2r\omega \sin \theta) = - \left\{ \frac{1}{3} \frac{d^2}{dr^2}(r^3 e) - 2re \right\} (2 \sin \theta \cos^2 \theta - \sin^3 \theta), \quad (14)$$

whence,

$$\frac{1}{r^2} \frac{\partial}{\partial \theta} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (2r\omega \sin \theta) \right\} = \frac{1}{r^2} \left\{ \frac{d^2}{dr^2}(r^3 e) - 6re \right\} \sin 2\theta. \quad (15)$$

Also,

$$\frac{\partial^2}{\partial r^2}(2r\omega) = - \frac{1}{6} \left\{ \frac{d^4}{dr^4}(r^3 e) - 6 \frac{d^2}{dr^2}(re) \right\} \sin 2\theta. \quad (16)$$

We have yet to express  $W$  in terms of  $r$ ,  $\theta$ , and  $e$  so as to substitute its value in (13).

Let  $P_2$  denote the spherical surface harmonic  $(\cos^2 \theta - \frac{1}{3})$ . Then

$$\epsilon = reP_2. \quad (17)$$

And by Routh's Statics, Part II. Art. 176, the potential of the earth's attraction at an internal point whose coordinates are  $r + \epsilon$ ,  $\theta$ , is

$$\begin{aligned} V &= 4\pi\gamma \int_r^a \rho r dr + \frac{4\pi\gamma r^2 P_2}{5} \int_r^a \rho \frac{de}{dr} dr \\ &\quad + \frac{4\pi\gamma}{r+\epsilon} \int_0^r \rho r^2 dr + \frac{4\pi\gamma P_2}{5r^3} \int_0^r \rho \frac{d}{dr}(r^5 e) dr \\ &= 4\pi\gamma \int_r^a \rho r dr + \frac{4\pi\gamma r^2 P_2}{5} \int_r^a \rho \frac{de}{dr} dr \\ &\quad + \frac{4\pi\gamma}{r} (1 - eP_2) \int_0^r \rho r^2 dr + \frac{4\pi\gamma P_2}{r^3} \int_0^r \rho \frac{d}{dr}(r^5 e) dr, \end{aligned} \quad (18)$$

where  $\gamma$  is the constant of gravitation and  $a$  the mean radius of the earth.

If  $m$  denotes the mass of the tide-producing body, and  $d$  its distance from the earth, the potential of its tidal action is

$$\frac{3\gamma m r^2}{2d^3} (\cos^2 \theta - \frac{1}{3}) = \frac{1}{2} h r^2 P_2 \quad \text{say,}$$

where  $h$  denotes the constant  $\frac{3\gamma m}{d^3}$ .

Now allowing for the convention of signs in gravitation potential we have

$$W = -V - \frac{1}{2}hr^2P_2, \dots \dots \dots (19)$$

Therefore,

$$\begin{aligned} \frac{\partial W}{\partial \theta} = \sin 2\theta \left[ \frac{1}{2}hr^2 + 4\pi\gamma \left\{ \frac{1}{5}r^2 \int_r^a \rho \frac{de}{dr} dr \right. \right. \\ \left. \left. - \frac{e}{r} \int_0^r \rho r^2 dr + \frac{1}{5r^3} \int_0^r \rho \frac{d}{dr}(r^5e) dr \right\} \right]. \dots (20) \end{aligned}$$

Now in the elastic equations the stresses expressed in terms of  $r$  and  $\theta$  are stresses in the element which was at  $(r, \theta)$  before strain, and is at  $(r+\epsilon, \theta+\eta)$  after strain. These stresses are in equilibrium with the applied forces at  $(r+\epsilon, \theta+\eta)$ . Now every term that contains  $\theta$  in  $W$  is a small term and consequently the difference between  $\theta$  and  $(\theta+\eta)$  can be neglected. In the third term in  $V$ , the only place where the difference between  $r$  and  $(r+\epsilon)$  is not negligible, account has already been taken of this difference. Therefore the expression on the right-hand side of (20) is

the proper expression for  $\frac{\partial W}{\partial \theta}$  in (13).

Substituting from (15), (16), and (20) in (13) we get, after dividing by  $\sin 2\theta$ ,

$$\begin{aligned} n \left[ \frac{1}{r^2} \left\{ \frac{d^2}{dr^2}(r^3e) - 6re \right\} - \frac{1}{6} \left\{ \frac{d^4}{dr^4}(r^3e) - 6 \frac{d^2}{dr^2}(re) \right\} \right] \\ - \frac{d\rho}{dr} \left[ \frac{1}{2}hr^2 + 4\pi\gamma \left\{ \frac{r^2}{5} \int_r^a \rho \frac{de}{dr} dr - \frac{e}{r} \int_0^r \rho r^2 dr + \frac{1}{5r^3} \int_0^r \rho \frac{d}{dr}(r^5e) dr \right\} \right] = 0 \end{aligned} \dots \dots \dots (21)$$

This is the differential equation which  $e$  has to satisfy ; and when  $\rho$  is given as a function of  $r$  the equation determines  $e$  as a function of  $r$ .

#### *The Boundary Conditions.*

We have yet to find the boundary conditions from which the constants are to be determined. The two conditions are, that the shear and the tension at the earth's surface, where  $r=a$ , are both zero. It should be remembered that  $r$  is not the distance from the centre of a particle of the strained sphere, but the distance of the particle before strain. Consequently,  $r=a$  exactly for a surface particle.

The shear strain in the plane of  $r$  and the symmetrical axis is

$$\frac{1}{r} \frac{\partial \epsilon}{\partial \theta} + r \frac{\partial \eta}{\partial r};$$

and since the shear stress is zero at the surface, it follows that the shear strain is also zero at the surface. Hence

$$\frac{1}{r} \frac{\partial \epsilon}{\partial \theta} + r \frac{\partial \eta}{\partial r} = 0 \text{ when } r=a. \quad (22)$$

This is one boundary condition.

The radial tension at any point is

$$(k - \frac{2}{3}n)\delta + 2n \frac{\partial \epsilon}{\partial r},$$

and this must be zero when  $r=a$ . But since  $n$  is infinitely small compared with  $k$ , and  $k\delta$  is finite, this condition can be written

$$k\delta + 2n \frac{\partial \epsilon}{\partial r} = 0 \text{ when } r=a. \quad (23)$$

This is the second boundary condition. It remains to express the two equations (22) and (23) in more convenient forms.

Substituting for  $\epsilon$  from (6) and for  $\eta$  from (9) in (22), we get ( $f(r)$  being dropped because it is zero)

$$-2e \cos \theta \sin \theta - \frac{1}{3} \cos \theta \sin \theta r \frac{d}{dr} \left\{ \frac{1}{r^2} \frac{d}{dr} (r^3 e) \right\} = 0$$

when  $r=a$ .

That is,

$$6e + r \frac{d}{dr} \left\{ \frac{1}{r^2} \frac{d}{dr} (r^3 e) \right\} = 0 \text{ when } r=a. \quad (24)$$

This is a very convenient form for the first boundary condition.

Now, since (23) is true for all values of  $\theta$ , we may differentiate all through with respect to  $\theta$ . Hence

$$k \frac{\partial \delta}{\partial \theta} + 2n \frac{\partial^2 \epsilon}{\partial \theta \partial r} = 0 \text{ when } r=a. \quad (25)$$

But since  $\delta$  is zero and  $n$  finite, the equation of equilibrium (12) may be written

$$k \frac{\partial \delta}{\partial \theta} + 2n \frac{\partial}{\partial r} (r\omega) - \rho \frac{\partial W}{\partial \theta} = 0. \quad (26)$$

This last equation is true at every point of the sphere, and

is therefore true when  $r=a$  for all values of  $\theta$ . Therefore any combination of equations (25) and (26) will be true all over the surface.

Subtracting (25) from (26), we get

$$-2n \frac{\partial}{\partial r} \left\{ \frac{\partial \epsilon}{\partial \theta} - r\omega \right\} - \rho \frac{\partial W}{\partial \theta} = 0 \text{ when } r=a. \quad (27)$$

Now equations (20) and (21) show that

$$\begin{aligned} \frac{\partial W}{\partial \theta} = & -n \frac{dr}{d\rho} \sin 2\theta \left[ \frac{1}{6} \left\{ \frac{d^4}{dr^4}(r^3e) - 6 \frac{d^2}{dr^2}(re) \right\} \right. \\ & \left. - \frac{1}{r^2} \left\{ \frac{d^2}{dr^2}(r^3e) - 6re \right\} \right], \quad (28) \end{aligned}$$

and this is the general expression for  $\frac{\partial W}{\partial \theta}$  at all points of the sphere. It can therefore be used in (27).

Also, from (6) and (10),

$$2 \frac{\partial}{\partial r} \left\{ \frac{\partial \epsilon}{\partial \theta} - r\omega \right\} = \left\{ \frac{1}{6} \frac{d^3}{dr^3}(r^3e) - 3 \frac{d}{dr}(re) \right\} \sin 2\theta. \quad (29)$$

Substituting from (28) and (29) in (27), and then dividing by  $n\rho \frac{dr}{d\rho} \sin 2\theta$ , we find

$$\begin{aligned} \frac{1}{6} \left\{ \frac{d^4}{dr^4}(r^3e) - 6 \frac{d^2}{dr^2}(re) \right\} - \frac{1}{r^2} \left\{ \frac{d^2}{dr^2}(r^3e) - 6re \right\} \\ - \frac{1}{\rho} \frac{d\rho}{dr} \left\{ \frac{1}{6} \frac{d^3}{dr^3}(r^3e) - 3 \frac{d}{dr}(re) \right\} = 0 \text{ when } r=a. \quad (30) \end{aligned}$$

For convenience, the other boundary condition is re-written here :

$$6e + r \frac{d}{dr} \left\{ \frac{1}{r^2} \frac{d}{dr}(r^3e) \right\} = 0 \text{ when } r=a. \quad (30 a)$$

We have to find  $e$  to satisfy equation (21) for all values of  $r$ , and equations (30) and (30 a) when  $r=a$ . These two boundary conditions are sufficient for the present problem. If we had been dealing with a hollow sphere, we should have had two more boundary conditions, and these are replaced in the present case by the condition that  $e$  must be finite at the centre.

### *Solution of the Equations.*

We can get no further without assuming an expression for  $\rho$ ; and to get a numerical result, we must assume a

value for  $n$ . Since it is generally asserted that the rigidity of the earth is about the same as that of steel, I shall give  $n$  the value  $8 \times 10^8$  grams per square centimetre, which is nearly the value for steel.

In order that the results may have any worth, the expression for  $\rho$  should be chosen so as to satisfy, as nearly as possible, all that we know about the earth's density. Thus we must make the mean density about  $5.5w$  and the density at the surface about  $2.5w$ , where  $w$  denotes the density of water. It will be found that both these conditions are satisfied by the equation

$$\rho = w \left( 10 - 7.5 \frac{r^2}{a^2} \right). \quad . \quad . \quad . \quad . \quad . \quad (31)$$

With this expression for the density, the differential equation (21) can be satisfied by taking

$$\begin{aligned} e &= A_0 + A_2 \frac{r^2}{a^2} + A_4 \frac{r^4}{a^4} + A_6 \frac{r^6}{a^6} + \dots \\ &= \Sigma A_m \frac{r^m}{a^m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (32) \end{aligned}$$

where  $m$  may be zero or any positive even integer.

That the boundary conditions can also be satisfied by this series will be seen in the course of the work.

Let  $x$  be written for  $\frac{r}{a}$ . Then on substituting for  $\rho$  and  $e$  in equation (21) we get, after multiplying through by  $a$ ,

$$\begin{aligned} \Sigma A_m \left[ 60\pi\gamma a^2 w^2 \left\{ \frac{1}{5} \left( 10 - 7.5 \frac{m}{m+2} \right) x^3 - \frac{10}{3} x^{m+3} + \frac{7.5}{5} \frac{m^2 + 9m + 4}{(m+2)(m+7)} x^{m+5} \right\} \right. \\ \left. - \frac{n}{6} (m-2)m(m+3)(m+5) x^{m-1} \right] + 7.5wha^2 x^3 = 0. \quad (33) \end{aligned}$$

By equating the coefficient of  $x^3$  in this to zero, we get

$$\begin{aligned} -\frac{2 \cdot 4 \cdot 7 \cdot 9}{6} n A_4 + 60\pi\gamma a^2 w^2 \left\{ \Sigma \left( 2 - \frac{3}{2} \frac{m}{m+2} \right) A_m - \frac{10}{3} A_0 \right\} \\ + 7.5wha^2 = 0. \quad (34) \end{aligned}$$

Also, when  $m$  is zero or any positive even integer, we find, by equating the coefficient of  $x^{m+5}$  to zero,

$$\begin{aligned} 60\pi\gamma a^2 w^2 \left\{ -\frac{10}{3} A_{m+2} + \frac{3}{2} \frac{m^2 + 9m + 4}{(m+2)(m+7)} A_m \right\} \\ - \frac{n}{6} (m+4)(m+6)(m+9)(m+11) A_{m+6} = 0. \quad (35) \end{aligned}$$

Now

$$\frac{4}{3} \pi\gamma a (5.5w) = g \text{ dynes.}$$

Hence

$$\frac{60\pi\gamma a^2 w^2}{n} = \frac{aw}{n} \frac{90}{11} g = \frac{637 \times 10^6 \times g}{800 \times 10^6 \times g} \cdot \frac{90}{11} = 6.51, \quad \dots \quad (36)$$

since  $a = 637 \times 10^6$  centimetres and  $n = 800 \times 10^6$  grams per square centimetre.

Let B be written for  $\Sigma \left( 2 - \frac{3}{2} \frac{m}{m+2} \right) A_m$ , and  $s$  for  $\frac{7.5wha^2}{n}$ . Then (34) gives

$$A_4 = \frac{6.51}{4.7.3} \left\{ B - \frac{10}{3} A_0 \right\} + \frac{s}{4.7.3} \\ = 0.07750 B - 0.2583 A_0 + 0.011905 s. \quad \dots \quad (37)$$

Also equation (35) gives

$$A_{m+6} = \frac{6 \times 6.51}{(m+4)(m+6)(m+9)(m+11)} \left\{ -\frac{10}{3} A_{m+2} + \frac{3}{2} \frac{m^2 + 9m + 4}{(m+2)(m+7)} A_m \right\} \quad (38)$$

when  $m$  is zero or any positive even integer. Putting  $m=0, 2, 4, 6$ , &c. in turn in this equation we get

$$A_6 = \frac{2.17}{4.3.11} \left\{ -\frac{10}{3} A_2 + \frac{3}{7} A_0 \right\} \\ = 10^{-5} \{ -5480 A_2 + 704.5 A_0 \}, \quad \dots \quad (39)$$

$$A_8 = \frac{6.51}{8.11.13} \left\{ -\frac{10}{3} A_4 + \frac{13}{12} A_2 \right\} \\ = 10^{-6} \{ -18970 A_4 + 6165 A_2 \} \\ = 10^{-6} \{ -1469 B + 4886 A_0 + 6165 A_2 - 225.7 s \}. \quad (40)$$

The last line is obtained by using the value of  $A_4$  from (37).

$$A_{10} = \frac{6.51}{10.13.20} \left\{ -\frac{10}{3} A_6 + \frac{14}{11} A_4 \right\} \\ = 10^{-6} \{ 247 B - 883 A_0 + 458 A_2 + 38.0 s \}, \quad \dots \quad (41)$$

$$A_{12} = \frac{6.51}{20.15.17} \left\{ -\frac{10}{3} A_8 + \frac{141}{104} A_6 \right\} \\ = 10^{-7} \{ 62.5 B - 86 A_0 - 1211 A_2 + 9.6 s \}, \quad \dots \quad (42)$$

$$A_{14} = \frac{6.51}{2.14.17.19} \left\{ -\frac{10}{3} A_{10} + \frac{7}{5} A_8 \right\} \\ = 10^{-7} \{ -21 B + 70 A_0 + 51 A_2 - 3.2 s \}, \quad \dots \quad (43)$$

$$A_{16} = \frac{6.51}{7.16.19.7} \left\{ -\frac{10}{3} A_{12} + \frac{97}{68} A_{10} \right\} \\ = 10^{-8} \{ 14 B - 54 A_0 + 46 A_2 + 2.1 s \}. \quad \dots \quad (44)$$



We have now to express  $B$  in terms of  $A_0$ ,  $A_2$ , and  $s$ . When this is done, we can express the coefficients  $A_4$ ,  $A_6$ , &c. in terms of two arbitrary constants  $A_0$  and  $A_2$ , and these can be found from the boundary conditions.

Thus

$$\begin{aligned} B &= \Sigma \left( 2 - \frac{3}{2} \frac{m}{m+2} \right) A_m \\ &= 2A_0 + \frac{5}{4}A_2 + A_4 + \frac{7}{8}A_6 + \frac{4}{5}A_8 + \dots \\ &= 0.0765 B + 1.751 A_0 + 1.207 A_2 + 0.01172 s, \end{aligned}$$

whence

$$B = 1.896 A_0 + 1.307 A_2 + 0.01269 s. \quad (45)$$

The substitution of this value for  $B$  in equations (37) and (40) to (44) gives

$$\left. \begin{aligned} A_4 &= 10^{-4} \{ -1114 A_0 + 1013 A_2 + 128.9 s \}, \\ A_6 &= 10^{-5} \{ 704.5 A_0 - 5480 A_2 \}, \\ A_8 &= 10^{-6} \{ 2101 A_0 + 4244 A_2 - 244.3 s \}, \\ A_{10} &= 10^{-6} \{ -415 A_0 + 781 A_2 + 41.1 s \}, \\ A_{12} &= 10^{-7} \{ 32 A_0 - 1130 A_2 + 10.4 s \}, \\ A_{14} &= 10^{-7} \{ 31 A_0 + 25 A_2 - 3.4 s \}, \\ A_{16} &= 10^{-8} \{ -26 A_0 + 65 A_2 + 2.4 s \}. \end{aligned} \right\} \quad (46)$$

We must now make use of equations (30) and (30a) to determine  $A_0$  and  $A_2$ .

The substitution

$$e = \Sigma A_m \frac{r^m}{a^m}$$

in equation (30) will give, after the differentiations have been performed

$$\begin{aligned} \Sigma A_m \left[ \frac{1}{6} m(m-2)(m+3)(m+5) \frac{r^{m-1}}{a^m} \right. \\ \left. - \frac{1}{6} \frac{1}{\rho} \frac{d\rho}{dr} (m+1)(m^2+5m-12) \frac{r^m}{a^m} \right] = 0 \quad (47) \end{aligned}$$

when  $r=a$ .

But since

$$\rho = \left( 10 - 7.5 \frac{r^2}{a^2} \right) w,$$

we see that, when  $r=a$ ,

$$\frac{1}{\rho} \frac{d\rho}{dr} = -\frac{1}{2.5} \frac{15}{a} = -\frac{6}{a}.$$

Hence, on substituting  $a$  for  $r$  in (47) and multiplying up by  $a$ , we arrive at the equation

$$\Sigma A_m [\frac{1}{6}m(m-2)(m+3)(m+5) + (m+1)(m^2+5m-12)] = 0. \quad (48)$$

That is,

$$\begin{aligned} -12 A_0 + 6 A_2 + 204 A_4 + 774 A_6 + 1972 A_8 + 4118 A_{10} \\ + 7596 A_{12} + 12854 A_{14} + 20404 A_{16} = 0. \end{aligned} \quad (49)$$

Using the values of  $A_4$ ,  $A_6$ , &c. from equations (46) we get

$$-26.78 A_0 - 5.004 A_2 + 2.322 s = 0. \quad . \quad . \quad (50)$$

Similarly the equation (30 *a*) gives

$$\Sigma A_m (m^2 + 3m + 6) = 0.$$

That is

$$\begin{aligned} 6 A_0 + 16 A_2 + 34 A_4 + 60 A_6 + 94 A_8 \\ + 136 A_{10} + 186 A_{12} + \dots = 0. \end{aligned} \quad (51)$$

By means of (46) equation (51) gives

$$2.78 A_0 + 16.64 A_2 + 0.421 s = 0. \quad . \quad . \quad (52)$$

The values of  $A_0$  and  $A_2$  determined from these equations are

$$\left. \begin{aligned} A_0 &= 0.0945 s \\ A_2 &= -0.0411 s \end{aligned} \right\} . \quad . \quad . \quad (53)$$

After expressing all the  $A$ 's in terms of  $s$  we find

$$\begin{aligned} e &= A_0 + A_2 \frac{r^2}{a^2} + A_4 \frac{r^4}{a^4} + \dots \\ &= 10^{-4} s \left\{ 945 - 411 \frac{r^2}{a^2} - 17 \frac{r^4}{a^4} + 29 \frac{r^6}{a^6} - 2 \frac{r^8}{a^8} + \dots \right\}. \end{aligned} \quad (54)$$

The ellipticity of the surface, obtained by putting  $a$  for  $r$  in (54), is

$$\begin{aligned} e_1 &= 0.0544 s \\ &= 0.0544 \times \frac{7.5 w h a^2}{n} . \quad . \quad . \quad (55) \end{aligned}$$

But since  $n = 8 \times 10^8$  grams per square centimetre,  $a = 637 \times 10^6$  centimetres, and  $w = 1$ ,

$$\frac{w a}{n} = \frac{637 \times 10^6}{8 \times 10^8 \times g} = \frac{0.796}{g}. \quad . \quad . \quad (56)$$



that is, the condition corresponding to (49), is large when  $m$  is large.

From (60) and (61) we get

$$e_1 = 0.321 \frac{ha}{g}, \quad . \quad . \quad . \quad . \quad . \quad (62)$$

which is very little different from the result in (57).

As both the results I have just obtained for the ellipticity are much smaller than the values given by Dr. Hecker's pendulums or by observations on ocean-tides, I have made another calculation with a smaller rigidity. In this case I have taken

$$\rho = w \left( 10 - 7.5 \frac{r^2}{a^2} \right), \quad . \quad . \quad . \quad . \quad . \quad (63)$$

$$n = 4 \times 10^8 \text{ grams per square centimetre,} \quad . \quad (64)$$

and I find

$$e = 10^{-4} \frac{ha}{g} \left\{ 7804 - 2683 \frac{r^2}{a^2} - 779 \frac{r^4}{a^4} + 404 \frac{r^6}{a^6} - 4 \frac{r^8}{a^8} \right. \\ \left. - 12 \frac{r^{10}}{a^{10}} + \frac{r^{12}}{a^{12}} \right\}, \quad (65)$$

and therefore the ellipticity of the surface is

$$e_1 = 0.473 \frac{ha}{g}. \quad . \quad . \quad . \quad . \quad . \quad (66)$$

Now a plumb-line would set itself perpendicular to the equipotential surface in its neighbourhood, that is, perpendicular to the surface which would bound an infinitely light liquid which may be imagined to cover the surface of the earth as far as the plumb-bob. There would be a tide on this light liquid similar to the tide on the ocean, but not exactly equal to the ocean-tide—except over the ocean itself. For, an ocean-tide depresses the solid earth beneath it to a slight extent, and moreover the attraction of the ocean-tide itself constitutes a tide-producing force. Both the depression of the solid earth and the mutual attraction of the waters would act in the same direction and make the ocean-tide larger than the tide on an infinitely light liquid extending down to the solid earth. The attraction of the Atlantic tide would have some slight effect on Dr. Hecker's pendulums at Potsdam, but it is considered small enough to be neglected. Now these pendulums really give the direction of the plumb-line relative to the solid earth; that is, they indicate the tide on the imaginary light liquid relative to the solid earth.

For when we know the position of the tide-producing body and the direction of the plumb-line, we can calculate the height of the tide on the equipotential surface relative to the solid earth, except of course when the tide-producing body is at the zenith or nadir of the point of observation, for then the deviation of the plumb-line is zero, since the crest of one of the tides is at the point of observation.

In order to compare calculated results with observations, it will be necessary now to find the ellipticity of the equipotential surface near the earth's surface and to subtract from this the ellipticity of the solid earth. This difference may be called the ellipticity of the equipotential surface relative to the earth.

Now the potential of the solid earth in the strained state at an external point ( $r'$ ,  $\theta$ ) is (see Routh's Statics, vol. ii. Art. 196)

$$V' = \frac{4\pi\gamma}{r'} \int_0^a \rho r^2 dr + \frac{4\pi\gamma P_2}{5r'^3} \int_0^a \rho \frac{d}{dr} (r^5 e) dr. \quad (67)$$

Since the second term in  $V'$  contains  $e$  and is therefore small, we may put  $a$  for  $r'$  in this term in the neighbourhood of the earth's surface. Also

$$4\pi\gamma \int_0^a \rho r^2 dr = ga^2. \quad (68)$$

Hence, near the earth's surface,

$$V' = \frac{ga^2}{r'} + \frac{4\pi\gamma P_2}{5a^3} \int_0^a \rho \frac{d}{dr} (r^5 e) dr. \quad (69)$$

But when

$$\rho = w \left( 10 - 7 \cdot 5 \frac{r^2}{a^2} \right), \quad (70)$$

we have found that

$$e = A_0 + A_2 \frac{r^2}{a^2} + A_4 \frac{r^4}{a^4} + \dots \quad (71)$$

Consequently

$$\begin{aligned} \int \rho \frac{d}{dr} (r^5 e) dr &= \rho r^5 e - \int r^5 e \frac{d\rho}{dr} dr \\ &= \rho r^5 e + \frac{15w}{a^2} \int r^6 e dr \\ &= \rho r^5 e + \frac{15w}{a^2} \left\{ \frac{1}{7} A_0 r^7 + \frac{1}{9} A_2 \frac{r^9}{a^2} + \frac{1}{11} A_4 \frac{r^{11}}{a^4} + \dots \right\}. \quad (72) \end{aligned}$$

Therefore, when  $n=8 \times 10^8$  grams per square centimetre,

$$\begin{aligned} \int_0^a \rho \frac{d}{dr} (r^5 e) dr &= 2.5 \, wa^5 e_1 + 15 \, wa^5 \left\{ \frac{1}{7} A_0 + \frac{1}{9} A_2 + \frac{1}{11} A_4 + \dots \right\} \\ &= 2.5 \, wa^5 e_1 + 15 \, wa^5 (90 \times 10^{-4} s) \\ &= 2.5 \, wa^5 e_1 + 15 \, wa^5 (0.1655 e_1) \\ &= 4.98 \, wa^5 e_1. \quad \dots \quad (73) \end{aligned}$$

The total potential near the earth's surface is

$$V' + \frac{1}{2} h r^2 P_2 = V' + \frac{1}{2} h a^2 P_2, \quad \dots \quad (74)$$

$a$  being written for  $r$  in the second term which is small.

Over an equipotential surface the expression in (74) is constant. That is,

$$\frac{ga^2}{r'} + \frac{4\pi\gamma P_2}{5} (4.98) wa^2 e_1 + \frac{1}{2} h a^2 P_2 = \text{a constant.} \quad (75)$$

But the mean density of the earth being  $5.5 \, w$  we find that

$$\frac{4}{3} \gamma \pi a (5.5 \, w) = g. \quad \dots \quad (76)$$

Hence, after being divided by  $ga$  (75) becomes

$$\frac{a}{r'} + \frac{3}{5.5} \frac{4.98}{5} e_1 P_2 + \frac{h}{2g} P_2 = \text{a constant.} \quad \dots \quad (77)$$

The constant in (77) depends on the particular equipotential surface we are dealing with. Since  $\frac{a}{r'}$  is nearly unity and the other two terms are small, the constant is also nearly unity for all equipotential surfaces near the earth's surface. For the particular equipotential surface with the same mean radius as the earth, the constant is exactly unity. Thus for this surface

$$\frac{a}{r'} = 1 - \left( \frac{3 \times 4.98}{5 \times 5.5} e_1 + \frac{h}{2g} \right) P_2.$$

And therefore

$$\frac{r'}{a} = 1 + \left( \frac{3 \times 4.98}{5 \times 5.5} e_1 + \frac{h}{2g} \right) P_2 \quad \dots \quad (78)$$

approximately.

The ellipticity of this surface is

$$\begin{aligned} \frac{3 \times 4.98}{5 \times 5.5} e_1 + \frac{ha}{2g} &= \left\{ \frac{6 \times 4.98}{5 \times 5.5} \times 0.325 + 1 \right\} \frac{ha}{2g} \\ &= 1.353 \frac{ha}{2g}. \quad \dots \quad (79) \end{aligned}$$

The ellipticity of this surface relative to the earth is

$$1.353 \frac{ha}{2g} - e_1 = 0.703 \frac{ha}{2g} \quad . \quad . \quad . \quad . \quad (80)$$

If the earth were perfectly rigid  $e_1$  would be zero and the relative ellipticity would be exactly  $\frac{ha}{2g}$ . Thus the relative ellipticity of the equipotential surface when the earth is about as rigid as wrought iron is 0.703 of what it would be if the earth were perfectly rigid.

With the same rigidity and the second expression, viz. the one in (58), for the density the relative ellipticity is found to be

$$0.705 \frac{ha}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$

which scarcely differs from the previous result. It appears then that variations in the law of density do not greatly affect the relative ellipticity, provided the mean density and the density at the surface are kept the same.

Assuming the conditions given in (63) and (64), the latter condition being that the rigidity is about half that of wrought iron, we find for the relative ellipticity of the equipotential surface

$$0.569 \frac{ha}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (82)$$

It is proved in Thomson and Tait's 'Natural Philosophy' (Art. 840) that the relative ellipticity, assuming the earth incompressible and of uniform density,  $5.5 w$ , is

$$\frac{19n}{11gaw} \cdot \frac{ha}{2g}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (83)$$

$$1 + \frac{19n}{11gaw}$$

the values of which are  $0.685 \frac{ha}{2g}$  and  $0.520 \frac{ha}{2g}$  when  $n$  has the values  $8 \times 10^6$  and  $4 \times 10^6$  grams per square centimetre respectively. The former value of the ellipticity should be compared with (80) and (81), and the latter with (82).

#### *Comparison with Observations.*

For a given position of the tide-producing body the deviation of the plumb-line from its mean position is proportional to the relative ellipticity of the equipotential surface and the

earth. Dr. Hecker has analysed the motion of his pendulums and has separated the effects of the sun and moon. But the variation of the temperature of the earth's surface in a solar day produces a distortion of the surface which gives rise to an apparent motion of the plumb-bob, the magnitude of which motion is several times as great as the motion due to the attractions of the sun and moon. This motion due to temperature is mixed up with that due to the sun's attraction since they have the same period and further very careful analysis is necessary to separate them. But the average temperature effect on a large number of lunar days is insignificant on account of the difference in period. For in a large number of lunar days the temperature effect will be positive and negative in nearly equal proportions so that it will disappear from the average. For this reason the lunar deviation is much more reliable than the solar deviation in calculating the rigidity of the earth.

It is shown in the article on "Tides" in the ninth edition of the *Encyclopædia Britannica* that the motion due to one tide-producing body, say the moon, may be analysed into two elliptic-harmonic motions whose periods are respectively a lunar day and half a lunar day. These ellipses vary with the declination of the moon. The linear dimensions of the diurnal ellipse are proportional to  $\sin 2\delta$ , and those of the semi-diurnal ellipse to  $\cos^2 \delta$ , where  $\delta$  denotes the declination of the moon. It follows then that the diurnal ellipse vanishes when the moon is in the equator, whereas the semi-diurnal ellipse has then its greatest dimensions.

Let  $\alpha$  and  $\beta$  denote the mean lengths of the axes of the lunar semi-diurnal ellipse calculated on the assumption of perfect rigidity. These would correspond to a relative ellipticity of the equipotential surface of magnitude  $\frac{ha}{2g}$ . If the actual relative ellipticity were  $f \frac{ha}{2g}$  the axes should be  $f\alpha$  and  $f\beta$ . Now the mean lunar semi-diurnal curve obtained from Dr. Hecker's observations, extending from December 1902 to May 1905, is an oval curve, approximately elliptical, with axes  $0.786\alpha$  and  $0.357\beta$ . The inequality of the coefficients has not yet been satisfactorily accounted for. The mean of the two coefficients  $0.786$  and  $0.357$  is  $0.571$ , and this may be taken as  $f$  to calculate the mean rigidity. In another series of observations extending from August 1905 to July 1907 the axes were  $0.586\alpha$  and  $0.400\beta$ . The mean of the coefficients in this case is  $0.493$ . Thus the earlier



series of observations indicates an ellipticity of the equipotential surface relative to the earth of magnitude  $0.57 \frac{ha}{2g}$ , and the latter series indicates an ellipticity of  $0.493 \frac{ha}{2g}$ . The former of these agrees almost exactly with the ellipticity in (82) calculated for the rigidity  $4 \times 10^8$  grams per square centimetre, rather less half the rigidity of steel. The latter ellipticity corresponds to a still smaller rigidity.

*Tidal Observations.*—The evidence from observations on ocean-tides is in very good agreement with Dr. Hecker's observations. Due to the moon's action there are two small tides with periods of a month and half a month respectively. It is considered probable that these long-period tides occur at the same places as the corresponding tides on the solid earth under the oceans. That is, these ocean-tides do not lag behind the solid tides to any appreciable extent. Suppose  $t$  is the calculated height of one of these ocean-tides on a perfectly rigid earth, the mutual attraction of the disturbed water being neglected. Now from a discussion of a large number of tidal observations W. Schweydar \* finds that the actual height of the tide is  $0.62 t$ . But assuming the density and rigidity which gave the result in (82), and allowing for the mutual attraction of the disturbed water as well as for the depression of the solid by the water-tide I have calculated that the height of the ocean-tide would be  $0.682 t$ . Now (82) shows that when the mutual attraction of the disturbed water and the depression of the solid is neglected, the height of the tide is  $0.569 t$ . In arriving at the result  $0.682 t$ , however, I have supposed that the ocean covers the whole earth, whereas it only covers about two-thirds of it. If we only allow, in the actual case, half the increase due to the mutual attraction of the water and the depression of the solid we get, as the height of the water-tide,  $0.625 t$ , which agrees almost exactly with the observed tide. Thus tidal observations also indicate that the rigidity of the earth is about half that of wrought iron.

#### *Evidence from Variation of Latitudes.*

If the earth is not spinning about its axis of greatest moment of inertia then, by theorems proved in rigid dynamics, its axis of rotation describes a cone in the earth itself with the axis of greatest moment of inertia as the axis

\* *Beiträge zur Geophysik*, Bd. ix. 1907.

of the cone. If the earth were perfectly rigid the axis of rotation would describe its cone in the earth in  $\frac{A}{A-C}$  days, where  $A$  is the earth's moment of inertia about its symmetrical axis and  $C$  its moment of inertia about an equatorial diameter. But if the earth behaved like a liquid its form would adjust itself so that the axis of rotation would be the axis of figure, and there would consequently be no wandering of the axis of rotation. Owing to the imperfect rigidity of the earth its form would partly adjust itself to the rotation so that the axis of figure at any instant is displaced from what we may call the permanent axis of figure towards the axis of rotation. If the instantaneous axis of figure is displaced a fraction  $f$  of the whole distance between the permanent axis of figure and the axis of rotation, then the latter axis will describe its cone in the earth in  $\frac{1}{1-f} \cdot \frac{A}{A-C}$  days. Now the quantity  $\frac{A}{A-C}$  is involved in the theory of the precession of the earth's axis, and observations tell us that its value is about 305. The shifting of the axis of spin would be manifested by an apparent variation of all latitudes. It is believed that observations do indicate a variation whose period is 430 days. A comparison of this with the calculated period gives  $f = 0.291$ .

The alteration of form of the earth is due to centrifugal force, and since this is similar to a negative tidal force, at least on an incompressible earth, it follows that calculations made for tidal forces can be applied to centrifugal forces also.

Now the distribution of land and water over the globe shows that the earth's figure is very nearly an equilibrium figure, and consequently we may assume that the extent to which the earth actually yields to the components of centrifugal force perpendicular to the permanent axis is the same as if the earth were liquid. The yielding of the earth a fraction  $f$  of what a liquid earth would yield indicates that it would yield to a tidal force to the same extent as to this periodic centrifugal force. Now owing to rotation the ellipticity of the earth's surface is known to be about  $\frac{1}{300}$ , and when centrifugal force is represented as a tidal force the quantity  $\frac{ha}{g}$  in our calculations is about  $\frac{1}{290}$ . Thus the earth, when behaving as a liquid, has an ellipticity  $\frac{290}{300} \frac{ha}{g}$ , and under the action of a tidal force of long period it has an ellipticity  $0.291 \times \frac{290}{300} \frac{ha}{g}$  or  $0.281 \frac{ha}{g}$ , according to

the observations of latitudes. A comparison of this with the results in (57), (62), and (66) leads to the conclusion that the earth is much more rigid than steel.

But the amplitude of the variation in latitude whose period is 430 days is only  $0''.15$  according to Chandler, a quantity which is within the limits of observation in determinations of latitudes. When it is remembered that two elaborate series of observations to determine the constant of aberration, namely those of Professor Doolittle of Philadelphia and Professor Rees of Columbia College, New York, give results differing by  $0''.09$ , it is clear that a large number of careful observations have to be reduced to discover a small variation of amplitude  $0''.15$ , or even to prove that it exists. Another drawback is that Chandler's reduction gives an annual variation with nearly as large an amplitude. Considering these things it is highly desirable that the existence of the 430-day variation of latitude should be confirmed by other evidence.

That such a variation of latitude should exist is very probable. It could arise from changes of form of the earth. These changes shift the earth's axis of greatest moment of inertia, so that, even if this axis once coincided with the axis of rotation the formation of a mountain system would cause a relative displacement. For example, the upheaval of the Himalayas and the Thibetan tableland from the general body of the earth might displace its axis of figure by over  $200''$ . If the upheaval took place slowly then the axis of rotation would be constantly pursuing the axis of figure in consequence of the viscosity of the earth and tidal friction, so that the angle between them would always be small\*.

But the variation of the axis of rotation itself causes the centrifugal forces (which are equivalent to a negative tidal force) to change their direction relative to the earth's body. If the axis of rotation is describing a cone in the earth's body then the alteration in the centrifugal forces causes a tide in latitude  $45^\circ$ . If we think of a spheroid as the surface of equilibrium under the earth's rotation, this spheroid always has the axis of rotation as its axis. If then the axis of rotation describes a cone of semi-vertical angle  $\theta$  about the earth's axis of figure in 430 days, then the ellipse of section of this spheroid by any meridian plane of the earth oscillates backward and forward in its own plane through  $2\theta$  in 430 days. This obviously causes a tide whose crest is in latitude  $45^\circ$ . To show this analytically let the earth's axis of figure be

\* See the paper "On the Influence of Geological Changes on the Earth's Axis of Rotation," Sir G. H. Darwin's *Scientific Papers*, vol. iii.

taken as axis of  $z$ , and let the axis of  $x$  be the equatorial radius in the plane of the axes of rotation and of figure. The direction-cosines of the axis of rotation are  $\sin \theta$ , 0, and  $\cos \theta$ ; and those of the radius through any point  $(x, y, z)$

inside the earth are  $\frac{x}{r}$ ,  $\frac{y}{r}$ ,  $\frac{z}{r}$ ,  $r$  being the radius vector.

Now the potential of centrifugal force at  $(x, y, z)$  is  $\frac{1}{2}\omega^2 p^2$  where  $p$  is the length of the perpendicular from  $(x, y, z)$  on the axis of rotation. But if  $\phi$  denotes the angle between the radius through  $(x, y, z)$  and the axis of rotation

$$\cos \phi = \frac{x}{r} \sin \theta + \frac{z}{r} \cos \theta,$$

therefore

$$\begin{aligned} p^2 &= r^2(1 - \cos^2 \phi) \\ &= r^2 - (x \sin \theta + z \cos \theta)^2. \end{aligned}$$

Hence the potential  $V$  of the centrifugal force is

$$\begin{aligned} V &= \frac{1}{2} p^2 \omega^2 \\ &= \frac{1}{2} r^2 \omega^2 - \frac{1}{2} \omega^2 \left\{ x^2 \sin^2 \theta + 2xz \sin \theta \cos \theta + z^2 \cos^2 \theta \right\} \\ &= \frac{1}{2} r^2 \omega^2 - \frac{1}{2} \omega^2 \left[ x^2 \sin^2 \theta + z^2 \cos^2 \theta + \sin \theta \cos \theta \left\{ \left( \frac{x+z}{\sqrt{2}} \right)^2 - \left( \frac{x-z}{\sqrt{2}} \right)^2 \right\} \right] \end{aligned}$$

The first term  $\frac{1}{2}r^2\omega^2$  is the potential of a radial force which causes no tide. Each one of the other terms represents a simple tide. The term  $-\frac{1}{2}x^2\omega^2\sin^2\theta$  denotes a negligible negative tide with its depressions on the  $x$ -axis. The term  $-\frac{1}{2}z^2\omega^2\cos^2\theta$  represents a negative tide with its depressions on the  $z$ -axis. This gives the mean bulge at the equator and does not shift relative to the earth. The expressions  $\frac{x+z}{\sqrt{2}}$  and  $\frac{x-z}{\sqrt{2}}$  are the perpendicular distances of  $(x, y, z)$  from the planes  $x+z=0$ , and  $x-z=0$ , and the corresponding terms in  $V$  give a positive and a negative tide in latitude  $45^\circ$ , the crests and the depressions all lying on one meridian circle, namely, the circle through the axes of rotation and of figure. Since the plane containing the axis of rotation is supposed to rotate in the earth about the axis of  $z$  in 430 days, it follows that the crest of one tide and the depression of the other will pass any place in latitude  $45^\circ$  once in every 430 days.

If the earth were perfectly rigid and the mutual attraction

of the tides were neglected, a force which has a potential

$$\frac{1}{2} \omega^2 \sin \theta \cos \theta \left( \frac{x-z}{\sqrt{2}} \right)^2$$

would raise a tide whose height (from low to high water) would be  $\frac{a^2 \omega^2}{2g} \sin \theta \cos \theta$ . Now since  $g = 290a\omega^2$ , we find that the height of this tide is  $\frac{a \sin 0'' \cdot 15}{580} = 0 \cdot 32$  inch if we take  $\theta = 0'' \cdot 15$ . This would be the actual difference of level of the ocean in latitude  $45^\circ$  due to the positive tide which results from the shifting of the earth's axis of rotation. For the circle of low water touches the parallels of latitude  $45^\circ$  north and south, and the crests are in the same latitude. Thus on each of these parallels there is high and low water separated by  $180^\circ$  of longitude. Consequently the change of level at any place in latitude  $45^\circ$  would be, on the preceding assumptions, the whole height of the tide,  $0 \cdot 32$  inch.

The negative tide lags behind the positive tide by half a period, and therefore its depression coincides with a point of low water of the positive tide. Thus the whole change of level due to the two  $45^\circ$ -tides would be  $0 \cdot 64$  inch.

But  $0 \cdot 64$  inch will not be the actual change of level if the earth yields to tidal forces. According to W. Schweydar, whose work has been referred to under 'Tidal Observations' in this paper, the actual height of a long period tide is  $0 \cdot 62$  of its theoretical height. This makes the change of level due to the  $45^\circ$ -tides become nearly  $0 \cdot 4$  inch. This is a measurable quantity, and if a tide of this height were found with a period of 430 days it would be strong confirmation of the result deduced from observations of latitudes.

It is useful to compare this tide with one of the long-period tides, for example, the monthly tide. It is shown in Art. 848 of Thomson and Tait's 'Natural Philosophy' that the mean change of level at the equator due to the monthly tide would be  $0 \cdot 87$  inch on a rigid earth. Thus the change of level due to the shifting of the earth's axis of rotation, assuming that this axis describes a cone in the earth whose semi-vertical angle is  $0'' \cdot 15$ , is nearly  $\frac{3}{4}$  of the change of level at the equator due to the monthly tide.

These  $45^\circ$  tides themselves would, in the course of time, bring the axes of rotation and of figure into coincidence, even without the assistance of the lunar and solar tides. But the rate of decrease of the angle between these axes differs so greatly for different assumptions concerning the effect of tidal friction that it does not seem very profitable to try to draw any conclusions from the results.

XLIX. *Electrical Experiments with Mercury contained in Tubes.* By J. H. VINCENT, M.A., D.Sc., A.R.C.Sc.\*

[Plates VI. & VII.]

INTRODUCTION.

**F**IVE luminous effects are dealt with in the following paper. They are :—

- (1) Persistent illumination in which a mercury arc increases and decreases in length rhythmically.
- (2) Periodic illumination in which the arc is intermittent.
- (3) Persistent illumination in which the arc is of constant length.
- (4) The emission of a faint bluish-green light from a space containing liquid mercury and its vapour.
- (5) Phosphorescence of fused quartz.

The first three of these are the chief matters to be discussed, and for brevity they will be referred to by the names (1) Necklace, (2) Fan, and (3) Ribbon effect respectively. These names indicate the appearance observed on viewing the arc in a revolving mirror whose axis of rotation is parallel to the tube in which the arc occurs. The fourth of the above effects will be called the Green Glow.

After trying a variety of methods of mounting the tubes, the plan of using Woulff's bottles provided with side tubulures near the bottom was tested. The tube was held horizontally between two such bottles, the side tubulures of which were fitted with rubber bungs, bored to receive the ends of the tube. This proved so convenient that it has been adhered to throughout most of the research. By connecting the spaces above the mercury in the bottles together and with a pressure- or exhaust-pump, the hydrostatic pressure of the fluid in the tube could be varied at will and measured on an open mercury manometer. The electric current was led to and from the apparatus by clean iron wires piercing bungs in the necks of the bottles and dipping into the mercury.

THE NECKLACE EFFECT.

If a capillary tube of quartz glass be mounted in this apparatus, it will generally be found possible, on filling the tube and lower parts of the bottles with mercury, to form the arc of rhythmically varying length in the tube. An adjustable resistance is placed in series, and the circuit

\* Communicated by the Author.

is completed by connexions with direct-current leads maintained at a potential difference of about a hundred volts. The arc may be struck by (a) externally heating the middle of the tube with a Bunsen flame or by an electrically-heated wire wrapped round the tube, (b) sending a sufficiently intense current through the mercury. The flickering intermittent light at first produced is succeeded, on suitably adjusting the resistance, by the arc of rhythmically varying length, which under favourable conditions appears to the unaided eye to be absolutely steady. On examining such an arc in a revolving mirror, it appears to be drawn out into a necklace-shaped band. A picture of such a band is shown in fig. 1 (Pl. VI.), which is a reproduction of a photograph taken on a moving photographic plate.

*Photographic Arrangements.*—In order to take photographs of the arcs on a plate moving with a known velocity, a camera was fixed so as to point vertically downwards. The space usually occupied by the dark slide was filled by a horizontal board, upon which the mounted tube or, as we may call it, the lamp was placed. The length of the tube was perpendicular to the direction of motion of the photographic plate; the light from the lamp, after traversing a slit in the board, passed downwards through the lens which focussed an image of the tube on the plate. The plate was carried by a trolley, running on the work-bench beneath the camera and actuated by a falling weight. The trolley moved in a light-tight tunnel of wooden planking, having a slit in it to allow the light from the lamp to reach the plate.

A Nernst glower placed behind a ring of holes in a rotating metal disk provided a time-signal marking fractions of a second on the moving photographic plate, on to which the light was directed by a reflecting prism and a lens.

The photograph (fig. 1) represents the necklace produced in a quartz tube 4 cm. long, 4.2 mm. external diameter, and .55 mm. internal diameter. The electromotive force in the circuit was 98 volts; the resistance in series with the lamp was 120 ohms. Similar particulars will be given for short arcs: 4 cm., 4.2 mm., .55 mm., 98 volts, 120 ohms. The current was about a quarter of an ampere, and the volts across the lamp 66. The hydrostatic pressure on the fluid in the tube was 78 cm. of mercury.

The line of lighter marks on the picture near the lower edge are the time-signals,  $\frac{1}{200}$  of a second apart, time progressing from left to right. These marks may not be clearly shown in the reproduction. Vertical distances on the picture represent lengths parallel to the axis of the tube

enlarged in the ratio of 14:13; this vertical scale is adhered to throughout all the photographs. The frequency, as calculated from the time-signals, is 72 complete periods a second.

It will be seen that the velocity of growth of the arc is greater than the velocity of decrement; the length of the interval of time occupied by the recession of the mercury columns being 12 per cent. less than the time of approach. Serrations and bright markings are seen on the upper side of the necklace in the negative. These are characteristic of the negative end of the arc. Similar marks are present in photographs of the ribbon effect, but not of the fan effect. These marks are probably due to the cathode being occupied only partially by the glowing patch of light, which is in continual motion. The effect is well known in connexion with ordinary mercury lamps.

Each enlargement or bead of the necklace pattern is marked by a pair of bright curved bands, symmetrical with respect to the horizontal line through the middle of the picture. These bands leave the waists as the arc grows in length, but they separate at a lower rate than the rate of recession of the mercury columns. When the arc has begun to decrease in length, the curved bands still separate until they meet the edge of the beads, when the period of approach is about one-third past. The band on the side nearer the anode is generally more distinct than the other; the parts of the figure outside these bands are darker than the parts within.

At first sight it would appear that these effects are due to the phosphorescence of the walls of the tube. This view is, however, disproved by noting that, in addition to its explaining the effect observed, it would also show that these bands should continue through the boundary of the beads and give bright curved markings outside the necklace.

These bands are probably due to the formation of a layer of mercury on the inside of the tube near the electrodes. In the case of the anode in the ribbon effect, as we shall find presently, a deposit of mercury dew is sometimes visible; but it is not necessary to have visible dew in order to get a fainter photographic effect: a very thin film of mercury dew might be quite sufficient to absorb the more actinic rays appreciably. The surface of the tube will be cooler than the vapour column, and will, when the mercury has just retreated, be cool enough to condense a layer of mercury. This coating of mercury will account for the darker portion outside the bands. The dew will evaporate as the heat from the middle portion of the arc travels outwards and heats the surface. This shows why the bands recede from each other. When the period of approach of the mercury columns has partly passed, the dew



will be reabsorbed by the tides of mercury as these move over the bedewed surfaces during the latter part of the period of approach. This shows why the curved bands meet the sides of the beads at an angle.

It should be noted that the part of the tube occupied by the waist of the necklace is filled with hot vapour, which expands outwards as the bead forms. In fact, there will be a hot wind blowing each way from the centre of the arc. In some photographs of necklaces, sharply defined narrow dark lines are seen following very similar paths to the curved bands. These are the tracks of globules of mercury, not large enough to fill the bore of the tube, as they are blown outwards by the hot mercury wind.

The mean position of the necklace remains at rest near the middle of the tube. The current may be reversed without extinguishing the lamp, but the mean position will now be nearer the new positive end of the tube. This is probably connected with the fact that in all mercury arcs the positive electrode tends to become hotter than the negative.

The behaviour of such a lamp as regards changes in external resistance, and in the electromotive force acting round the circuit, can be shown on a diagram such as Pl. VII. fig. 2, in which the ordinates are proportional to the external resistance and the abscissæ to the electromotive force. On such a diagram there is an area ABC indicating the ranges of volts and ohms within which the necklace is produced. Between the lines AB and DE the necklace is not perfect, but has a very thin waist, which is occasionally broken. Above DE the lamps will not keep alight. All along AB the necklace is characterized by having a very thin waist; while along AC the waist is very wide. Just below AC the necklace is imperfect, the luminosity usually ceasing while the arc is growing in length.

The changes due to altering the external resistance are shown in the photographs, Pl. VI. figs. 3, 4, & 5, taken with the same tube as fig. 1, and with approximately the same voltage but different resistances. With too little resistance (30 ohms), the effect is as shown in fig. 3. The broken necklace pattern is varied by the occasional presence of a fan. The invariable characteristic of the arcs produced in regions in the diagram indicated by points below line AC, is that the arc is never maintained until the columns come into contact. It usually ceases to be luminous while still growing in length. As the resistance is increased, we get figures approaching more and more nearly to the typical necklace pattern (fig. 1). The necklace finally becomes perfect, and remains so until we cross the line AB, when the waists, previously quite thin, now occasionally break. This is shown in fig. 4, in which

the resistance was 190 ohms. The first bead shows a stationary drop of mercury left in the tube, which is re-absorbed into one of the columns of mercury as the waist is formed. The explosion which initiates the last bead but one also leaves a pair of drops of mercury in the tube near the cathode. These move outwards and are met by the return column.

All else being maintained as before, the resistance was raised to 600 ohms and fig. 5 taken. The width of the beads and waists is now greatly reduced. We are now approaching the line DE (fig. 2), and the lamp would be extinguished by raising the external resistance much beyond this limit. The invariable characteristic of the arcs produced in regions in the diagram indicated by points above AB and below DE, is the presence of arcs that keep lit until the columns unite.

Approximate straight lines like DE, AB, and AC form the typical diagram showing the connexion between the external resistance and the electromotive force in the necklace effect. When the pressure on the fluid is raised considerably, the lines are convex to the axis of volts. With the temperature of the laboratory maintained constant, it is possible to obtain very concordant series of readings for the circumstances governing the production of the necklace effect in any given tube, due care being taken to maintain the total hydrostatic pressure on the fluid in the tube constant. This concordance, in general, is only found among the numbers obtained from a particular mounting of the tube. Even when the attempt is made to fill the perfectly dry tube with pure dry mercury, and to remove all the air from the tube, differences in the diagram are found with each filling. The most pronounced difference in the behaviour of a tube with separate fillings, each performed with great care, is shown in Pl. VII. fig. 6, 10 cm., 3.9 mm., .36 mm., 81 cm. pressure, in which the lines DE, AB, AC refer to one filling, and *ab*, *ac* refer to another. In this latter case the line *de* was only indicated by the fact that in the neighbourhood of the point *a* it was possible to get the necklace to break at the waist without the lamp being extinguished altogether; with higher voltages, the lamp went out while still showing a good necklace when the resistance was raised too high.

From the diagrams (figs. 2, 6, & 7) we shall see that, with different lengths of tube and at different pressures and with different fillings, the perfect necklace region is always bounded by two lines rising from left to right. From other diagrams showing the behaviour of tubes of different bore, not here reproduced, it was found that this applies also to variation in internal diameter.

The change in the diagram due to alteration in length of tube is shown in fig. 2, in which AB, AC, DE refer to a tube 4 cm. long, and *ab*, *ac* to a tube of the same external and internal diameter, but 20 cm. long. The line *de* was unrepresented in the latter case. The shorter the tube, the less the resistance required to give a good necklace on any given voltage. Further, the shorter the tube, the lower the minimum possible voltage for the production of the necklace.

The diagrams (figs. 2, 6, & 7) all refer to tubes having the same internal diameter. If the other circumstances are kept constant, but the internal diameter is increased, the effect is to make the lines AB and AC become less sloped to the axis of volts, and to make the angle BAC less also. Increasing the internal diameter makes the allowable range of resistance less on any voltage, and also necessitates the actual resistance being made less.

If all else be kept the same, an increase in hydrostatic pressure necessitates a decrease in external resistance on any given voltage. This is shown in fig. 7, in which AB, AC are the necklace limits for 81 cm. pressure, and *ab*, *ac* are the corresponding limits when the pressure is raised to 162 cm. These results were obtained with the same filling of the tube, this tube being the same as that used in fig. 6.

Having referred to the general character of the changes in the diagram produced by varying the length and bore of the tubes and the mean hydrostatic pressure on their contents, the changes in the frequency, current, fall of potential, and length of arc must be dealt with.

The frequencies have usually been determined by stroboscopic means. The speed of rotation of the disk was determined by a mechanical counter and a stop-watch, and was regulated by a rheostat in series with the electric motor. An electromagnetic eddy current break was subsequently fitted to the instrument, to serve as a fine adjustment to the speed. The axle which bore the stroboscopic disk also carried a four-sided reflecting prism, and the tubes could be placed parallel to the axis of rotation. By means of a photographic lens, a real image of the tube was thrown, after reflexion, on to a ground-glass screen. The apparently stationary image thus produced could be studied in detail; the method was found useful in tracing the gradual changes in the phenomena as the circumstances were arbitrarily varied. In the necklace effect, the image on the screen can be kept quite still, showing that the phenomena are of very regular periodicity.

In all the cases which have been investigated, the frequency falls as the indicating point moves from A to B. Thus in

fig. 2, as the volts change from 78.5 to 364 and the external resistance from 190 to 2690 ohms, the frequency changed from 77 to 63 per second. The mean current (as read by a moving-coil instrument) falls slightly from .135 to .12 ampere, the root mean square volts across the arc (as read by a Kelvin electrostatic voltmeter) rise from 55 to 80. The maximum width of the bead changes from 1.4 to 1.7 cm. while the mean voltage drop per cm. of arc-length increases from 75 to 91. Similar changes occur in all necklace lamps as we pass from A to B.

As one alters the volts and resistance so as to keep the necklace unbroken on the lowest resistance for each voltage, *i. e.* along lines like AC, the frequency may either decrease or increase. When the internal diameter is about .35 mm., tubes less than about 7 cm. in length show a rise in frequency from A to C; tubes longer than this show a fall in frequency from A to C. The mean current rises from A to C when the frequency rises, and falls in those cases in which the frequency falls. The mean current and frequency are closely interdependent. This is because, as will be shown later, much of the electrical energy supplied to the lamp is employed in overcoming the viscous resistance of the mercury.

The arc-length affects the frequency in two ways: first, when the mean arc-length increases, the mean mass of mercury to be moved is lessened; second, the arc behaves (under the same mean current) as a gas having a variable pressure which rises when the arc shortens—in fact, the pressure exerted by the gas in the arc is not independent of the volume and cannot be simply regarded as saturated mercury vapour.

In spite of the complicated interactions occurring in the necklace effect, some approximate rules governing the frequency may be given.

The frequency in the neighbourhood of the point A in the different diagrams is roughly inversely as the square root of the length of the mercury columns.

On 200 volts:

Length of Tube, L.	Length of Arc, A.	Difference, L - A.	Frequency, F.	$F \cdot \sqrt{L - A}.$
4	.8	3.2	70	125
4	1.5	2.5	76	120
10	1.0	9.0	35	105
10	1.6	8.4	34	98
10	.6	9.4	39	119
10	1.3	8.7	37	109
20	.5	19.5	27.5	121
20	1.3	18.7	27	117

Thus in the table above with different lengths of tube, all of the same bore and external diameter, on 200 volts the product of the frequency and the square root of the mean reduced length of the mercury in the tube is approximately constant.

With the same tube and the same filling, the frequency varies directly as the square root of the mean pressure.

Length of tube 10 cm. :

E.M.F. in circuit.	Pressure in cms. of mercury. P.	Frequency. F.	Limit of Resistance.	Nos pro- portional to $\frac{F}{\sqrt{P}}$ .
200	81	39	upper	39
	162	55		39
	81	37	lower	37
	162	52		37
300	81	38	upper	38
	162	53		38
	81	36	lower	36
	162	49		35
400	81	39	upper	39
	162	51		36
	81	36	lower	36
	162	47		33

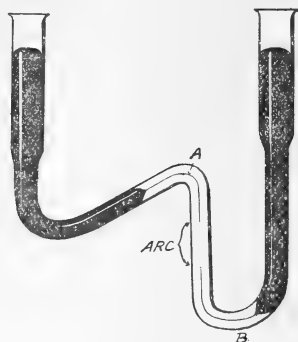
Thus in the above table if one compares the frequencies at corresponding points on the two diagrams of fig. 2 ( $f$  corresponding to  $F$ ,  $g$  to  $G$ ), it is seen that this rule is obeyed at low voltages, but is less closely followed at higher voltages.

It follows that if we regard the motion as a maintained harmonic motion, the corresponding inertia is proportional to the length of the tube less that of the arc, and the "spring" is proportional to the pressure.

It is not necessary to have the tube straight or horizontal, or to have a large mass of mercury in order to obtain the necklace effect. A quartz vessel was constructed as shown in fig. 8 (p. 514). The capillary portion was 6.6 cm. long, and had a mean internal diameter of .38 mm. The arc occupies the portion indicated in the figure. Without any auxiliary heating, this lamp would start sparking with a current of 4.1 amperes. The volts across the lamp just previous to lighting measured about 3, so that the resistance of the thread of mercury when on the point of breaking was about three-quarters of an ohm. On 100 volts this lamp required a resistance of about 420 ohms to produce the necklace, the width of the beads being 1.3 cm. and the frequency 55.5. The current was .08 ampere. On 200 volts and 1720 ohms,

the lamp took  $\cdot 075$  ampere, and the extreme length of the arc was 1 cm. With 1420 ohms, the current fell to  $\cdot 06$ , the width of the beads increased to 1.8 cm., and the waists were now  $\cdot 4$  cm. long. The root mean square volts across the lamp were 107.

Fig. 8.



It is possible to employ glass capillary tubing in experimenting on the necklace effect. Initial trouble may be experienced owing to the gases disengaged from the walls of the tube. If these preliminary difficulties are patiently dealt with, it will be found possible to run such glass lamps for a considerable time. A soda-glass tube (7 cm., 6.1 mm.,  $\cdot 45$  mm.) ran for an hour, giving a fairly steady light on 104 volts, after which the experiment was discontinued. Soda-glass lamps end their lives by cracking; the cracks commence internally and spread radially. Lead-glass tubes seal up, the bore of the tube becoming filled with an apparently crystalline black opaque mass. The cracking is not so marked as in the case of soda glass. Quartz tubes do not deteriorate appreciably when used in necklace lamps. Internal staining of the tube sometimes occurs, which may disappear on further use. This staining is less the purer the mercury, and is probably due to the presence of impurities.

Tubes of much larger internal diameter than can be employed for the production of the necklace effect when surrounded by air can be used if plunged into cold water.

#### THE FAN EFFECT.

Having described some of the phenomena occurring in the part of the diagram fig. 2 between the lines DE and AC, the area below AC must be investigated.

The experiments on this region are difficult, because even quartz tubing will not withstand the battering and explosive action of the sparks. Above AC the life of a quartz tube is, as far as one can tell, unlimited; below AC, *i. e.* when the luminosity ceases while the mercury thread is broken, the life is short, and becomes shorter the nearer we approach the axis of electromotive force. Another experimental difficulty is that the lamps are always liable to go out, and cannot be kept alight long enough to be studied in detail. The observer may easily over-estimate the regularity of the luminous phenomena met with in this region if he judges by the appearance of the stroboscope and not by the image of the sparks shown, after reflexion from the revolving mirror, on the screen. Even when the stroboscope is showing a well-defined frequency the appearance on the screen may be very irregular. If the stroboscope rings are marked out in equal angular parts of black and white, so long as the periodicity is fairly regular, the disk may appear still; the mirror is a much more severe test of regular periodicity.

It is only when very narrow tubes are employed that the periodicity is sufficiently well marked as to allow of continuous study of the effects in the rotating mirror. With wider tubes the effects are irregular, though sufficiently periodic to allow of frequency determinations with the stroboscope. Even with these tubes, however, the lamp on starting (either by external heating or by the use of a large current) exhibits very regular phenomena. These initial regular phenomena may be regarded as constituting the typical fan effect photographed in figs. 9, 10, and 11 (Pl. VI.).

In fig. 9 the time signals shown faintly near the lower edge of the picture are '006 second apart. The tube was of soda glass (9 cm., .4 mm. bore). The current was obtained from a dynamo, the electromotive force being 108 volts, the resistance being 37 ohms. Horizontal lines on the picture represent opacity or refractive defects in the tube. On the negative faint vertical marks are seen towards the right of each fan pattern due to small changes in the current owing to the electromotive force of the dynamo varying as the armature revolves. This point will again be referred to. It will be seen that the luminous interval occupies about a sixth of the whole period. Some photographic experiments undertaken in order to record the motion of the mercury in the fan effect, apart from the luminosity, have not proved successful; but from the occasional presence of a necklace pattern in a series of fans seen in the revolving mirror, one may be assured that even in the typical fan effect

the motion of the mercury is of the necklace type, but the interval of approach is in the fan effect much longer than the interval of recession, this being only very slightly longer than the luminous period. The time during which the columns are united is also probably a small fraction of the period, so that nearly the whole time of darkness is occupied by the mercury columns in again coming together to fill the tube.

The history of the growth of the arc is shown in the picture. It commences with a finite length, grows slowly with increasing velocity until after about a thousandth of a second the velocity of growth is constant, and remains sensibly so until the arc goes out.

Fig. 10 (Pl. VI.) gives a photograph obtained with a lead-glass tube (9 cm., .27 mm. bore). This took a mean current of .25 ampere in series with 37 ohms on 105 volts. The time signals are .005 second apart, which scale is adhered to throughout the remainder of the photographs. It will be seen that the luminous interval is not the same for each fan pattern. The dark striæ due to the lack of uniformity in the electromotive force are again visible.

In fig. 11 we have an example of the column breaking in two places. The upper arc is seen to move along the tube at a rate approximately equal to the rate of growth of the length of the main arc in the same direction. This would seem to show that in this case, at least, the mercury in the tube on each side of the main arc moved as a whole; and the growth of the arc was accompanied by an expulsion of some of the mercury from each end of the tube. One may also regard it as possible in some cases that mercury vapour is present at other places than the portion of the tube occupied by the arc, the growth of the arc being accommodated by the condensation of this vapour as the mercury recedes from the centre of the tube. It will be noticed that the healing of the upper column, due to the collapse of the smaller arc, is simultaneous with the sudden increase in luminosity shown by the bright vertical band in the lower fan. The photograph fig. 11 was obtained with a lead-glass tube (9 mm., .24 cm. bore). The volts on the mains were 110 and the current was .2 ampere with 23 ohms in series.

The phenomena exhibited by any tube on a given voltage do not change suddenly as we decrease the resistance so as to cross the line AC. The frequency, mean current, and mean volts across the lamp do not change suddenly. The test of having descended below AC is that the arc may go out with the columns still separated. As we decrease the resistance



the change becomes more noticeable. The period of luminosity becomes a smaller and smaller fraction of the whole period, until in the typical fan effect it may be as small as  $1/25$ . In all the cases that have been examined, this is the characteristic feature of the portions of the diagrams below AC, and in all cases except those of very fine tubes, the statement may be made that the arc goes out while the columns are still separating.

As in the case of the necklace effect, increasing the length of the tube lowers the frequency. The relation between frequency and length is not, however, the same in the two cases. In the necklace effect, the length of the tube is practically a measure of the moving mass in a motion which is approximately simply harmonic. In the fan effect the periodic time is only slightly greater than the period of approach, and is thus largely dependent upon the time required for a column of mercury to grow a certain small length when subjected to a constant difference of pressure between the two ends. In this case the internal pressure between the columns drops to a negligible quantity as soon as the arc goes out. So that we should expect that with different tubes, but under the same conditions of external resistance and pressure and on the same voltage, the frequency would vary approximately as the reciprocal of the length. Several series of results bear out this view. The longest series is given below.

Soda-Glass Tubes. .35 mm. bore, 6 mm. external diameter,  
56 ohms in series, 105 volts across direct current mains.

L.	F.	L.F.
3	100	300
4	78	312
5	59	295
6	55	330
7	48	336
8	44	352
9	40	360
10	38	380
12.5	33	412
15	28	420
20	24.5	490
25	22	550
30	21	630
35	20	700

As a second approximation LF is a linear function of  
*Phil. Mag.* S. 6. Vol. 22. No. 130. Oct. 1911. 2 M

$L$  or  $F = \frac{C}{L} + K$ , where  $C$  and  $K$  are constants. This

equation represented very closely the results obtained in this series of experiments and of other series of the same type. Changing the bore of the tube has very little effect on the frequency.

Experiments on the effect of change of pressure on the frequency led to the result that the frequency was not proportional to the square root of the pressure as in the necklace effect; but was approximately proportional to a power of the pressure greater than .5. With a narrow tube (.1 mm. bore) the frequency varied very nearly as the pressure to the power .86. Three series of experiments on the change of frequency with pressure are shown in fig. 12 (Pl. VII.). Curve A gives the results for a quartz tube (4.9 cm., 6.4 mm., .23 mm., 105 volts, 51 ohms). Curve B shows those for another piece of the same tube 10 cm. long, 103 volts, 37 ohms; while curve C refers to a quartz tube (5 cm., 5 mm., .1 mm., 112 volts, 101 ohms).

In the last case careful observations were made of the appearance of the arcs on the screen after reflexion from the revolving mirror as the pressure was changed. When the pressure was much below 29 cm. the intermittent arcs tended to give place to a steady arc which will be considered later under the "ribbon" effect. When the pressure was 29 cm. the appearance was that of fig. 9, the arcs being very regular both in size and in periodicity. The period of luminosity was 1/10 of the whole period. As the pressure was increased, the period of luminosity increased relatively to the whole period, and became 1/9 at 44 cm. and 1/6 at 79 cm. pressure. The fans meanwhile were getting less wide, that is, the maximum arc length decreased. At 109 cm. the arcs show a phenomenon which is only met with in very narrow tubes: they go out while the threads of mercury are still approaching. In this case the luminous fraction of the period is about 1/4; more often they cease to be luminous when the maximum width has been reached, and then the fraction is about 1/5; but on this pressure the fans are occasionally replaced by necklace figures in which the arc breaks on growing as in fig. 3. As the pressure is increased, the fans become less frequent and the broken necklaces become more frequent until at 160 cm. the latter predominate.

The effect of altering the electromotive force on the frequency is shown in fig. 13 (Pl. VII.), in which the curves  $a$ ,  $b$ ,  $c$ ,  $d$  refer to sets of experiments on different tubes. The dimensions of the tubes and the magnitude of the external resistances

were: (a) lead glass, 4 cm., 5.8 mm., .26 mm., 1 ohm; (b) quartz, 3.7 cm., 5.3 mm., .22 mm., 38 ohms; (c) quartz, 3 cm., 5.3 mm., .3 mm., 2 ohms; (d) quartz, 3.5 cm., 4 mm., .46 mm., 5.25 ohms.

*Effect of Resistance of Circuit on Frequency.*

The frequency is not greatly affected by changing the external resistance in the fan effect. Thus in a series of experiments with a quartz tube (11 cm., 5.3 mm., .35 mm., 95 volts) the resistance in series with the tube was changed step by step from 12 to 111 ohms. The frequency rose from 34 to 39. The effective resistance of the tube (calculated from the mean current observed) rose meanwhile from 240 to 570 ohms.

*Experiments with Self-Induction in Series with the Tube.*

Hitherto the self-induction in the circuit has been reduced as far as possible. If the circuit is made inductive, interesting intermittent luminous effects may be obtained by the use of a few accumulators only.

Gernsback (Scientific American, xciii. p. 82, July 29th, 1905) has described an apparatus of this type intended as an interrupter for small induction-coils. A glass capillary U-tube of 1/8 mm. bore is provided with enlarged ends, filled with pure mercury and immersed in water. With 4 to 6 volts this tube acts as an interrupter and gives a high-frequency note. It allows from .25 to .5 ampere to pass, and was used in connexion with the condenser of the coil. Higher voltages caused the interrupter to work irregularly.

Experiments in which the self-induction of the circuit is large are not always successful: great care must be taken to rid the tube and mercury of foreign matter. A soda-glass tube (10 cm., 7.2 mm., .97 mm.) was set up with the bottles serving as mercury reservoirs as usual. After running for some time without self-induction, on three large accumulators in series, it had a period of about 30 seconds, during a third of each period the column was unbroken. A resistance of one-tenth of an ohm wound non-inductively was removed from the circuit, and an inductive coil of the same resistance wound on laminated iron inserted in its place. This iron formed an open magnetic circuit for the coil, the self-induction of which, measured with an alternating current of about five amperes (frequency 60) was 2.5 millihenries. The central part of the tube lit up brilliantly on inserting the self-induction, but the light ceased after a few seconds, and left

the tube with the mercury not in electrical contact. After some further trouble with the disengagement of gas, the tube again lit up and kept alight for four minutes when the tube failed. The frequency was 38.5; it took a mean current of 3 amperes. A similar tube of soda glass ran successfully for 8 minutes, and others (jacketted with wider glass tubes) for 17 and 20 minutes respectively before the tube failed.

A quartz tube (10 cm., 4.3 mm., .46 mm.) ran very satisfactorily as a low voltage mercury lamp. When in series with the above coil and a moving coil voltmeter shunted with one ohm, the mean current from three large accumulators in series was .5 ampere. A soft-iron voltmeter was connected to the lamp terminals; this read 6 volts, the reading of the same instrument on the cells alone was 6.2 volts. The light occupied about 2 mm. length of the capillary bore in the middle part of the tube, and was of a white colour with a very faint bluish tinge. When the lamp was first lit, it had a frequency of 106 which gradually rose until when about 117 the lamp went out. This phenomenon could be repeated as often as desired. By removing the shunted voltmeter from the circuit, the resistance external to the lamp was practically reduced to that of the inductance coil, *i.e.* .1 ohm. This alteration had the effect of rendering the light permanent. The lamp continued to give out a bright pleasant light until the current was switched off. Under the new conditions the soft-iron voltmeter across the lamp read 6.5 volts.

A telephone receiver connected in series with 12,000 ohms across the lamp gave out a somewhat raucous deep note corresponding to the frequency of the lamp; the octave of this note was also present. Inserting small resistances in the lamp circuit raised the frequency. By gently heating the middle of the tube with the flame of a Bunsen burner, the frequency was lowered. Stronger heating caused the lamp to emit the green glow. The green light was given out by the capillary for a length of about 1.5 cm. on each side of the bright star of light in the centre of the tube, but separated from it by about 2 cm.

Similar experiments were performed with another quartz tube (6.15 cm., 5.5 mm., .4 mm.). This tube gave a bright intermittent arc about 1.5 mm. long at its centre when run from five large accumulators in series. In addition to the inductance coil, the resistance of which was .1 ohm, 2.09 ohms extra resistance was needed to get the best effect. Thus the resistance in the circuit in addition to that of the lamp was about 2.2 ohms. The mean current was .6 ampere, and a

soft-iron voltmeter read 9.5 volts across the lamp and 10.2 on open circuit. The frequency was 120. This tube also gave the green glow on each side of the arc on heating with a flame.

By rapidly changing the number of cells in the circuit, it was noticed that raising the volts lowered the pitch; and it was again found that raising the resistance external to the lamp raises the pitch. A telephone receiver arranged as a shunt on the lamp was used in these experiments. If 400,000 ohms are in series with the receiver a more musical note is produced than with a lower resistance.

*Fan Effect not always due to Contact and Separation of  
the Columns of Mercury.*

This will be a convenient place to record a very puzzling observation which must be taken into account in forming any theory of the fan effect. Using a quartz tube (10 cm., 4.3 mm., .46 mm., 100 volts) the mean current and resistance in the circuit were noted. The central portion of the tube was heated by the flame of a Bunsen burner which was kept in the same position during the following experiments. A frosted glow-lamp was placed behind the tube so that by looking at the tube in the direction of the illuminated lamp globe through a piece of flashed ruby glass, the position of the mercury in the tube could be seen.

The tube is occupied by the liquid mercury with the exception of a space two or three centimetres long over the Bunsen flame. The part of the tube thus chiefly occupied by the mercury vapour was not of fixed length, but was rapidly changing, and its ends on either side gave out the green glow. The middle portion of the tube was not, however, quite free from liquid mercury, a few very small particles being visible in the middle of the tube. As the resistance external to the lamp decreased, it became impossible to see these globules owing to the glare from the middle portion of the tube which became brilliantly luminous as the current increased. But on either side of the flashes of light the tube appeared to be free from liquid mercury. When the current was small, the middle portion contained a number of microscopic scintillations. Unless a magnifying glass be employed these tiny sparks appear to occur in the middle of a mass of vapour; the colour of these sparks looked white in contrast to the green glow from the ends of the vapour column. By the use of the revolving mirror it was observed with surprise that the bright central light was of the usual fan form. Up to this stage in the research the

fan effect had been looked upon as the consequence of the contact and retreat of the two halves of the broken mercury column. These observations show that whether or not this is the case normally, it does not represent the only conditions which will produce the fan effect.

The readings for mean current and external resistance are given in the table below, the last column of which gives the effective resistance of the lamp calculated from the numbers in the first two columns. The electromotive force was 100 volts throughout.

Current.	External Resistance.	Effective Resistance of Lamp.
·05	111	1890
·14	56	659
·18	34	518
·25	28·5	372
·30	23	310
·32	20	295
·35	17	269
·40	15	235
·45	13	208
·48	12	196
·55	10	172
·60	9	158
·65	8	146
·68	7	140
·73	6	131
·80	5	120

The experiment was brought to a close by the explosion of the tube. The effective resistance of the lamp rises rapidly with increase in the external resistance. The drop of volts in the lamp, calculated from the numbers in the first two columns, varies only between 92·2 and 96, this latter being the value for the greatest current.

#### THE RIBBON EFFECT.

By increasing the frictional resistance to the motion of the mercury in the tube, it is possible to obtain an arc of constant length in mercury vapour under approximately atmospheric pressure.

This is the principle of a mercury-vapour lamp described by Kent, Lacell, and the Silica Syndicate Limited (British Patents Nos. 5596, 21834, 1908). This lamp consists of a quartz tube initially filled with mercury. The column of mercury is broken by a subsidiary heating coil in order to start the lamp. Reservoirs of mercury at each end of the tube

communicate with it by constricted openings; this steadies the liquid and prevents rapid oscillations of the columns. In such lamps difficulty arose owing to the hotter electrode becoming depleted of mercury which deposited on the cooler negative electrode, so that the arc gradually passed towards the positive end of the tube. This was overcome in a very elegant manner by so forming the tube of the lamp that the part where the positive electrode is situated is brought near to or is made to touch the portion occupied by the negative end of the arc. The difficulty could also be overcome by employing a suitably placed subsidiary heating coil.

The author is indebted to Mr. H. G. Lacell for further information about these lamps. They are usually constructed to operate on a 500 volt circuit, but lamps suitable for lower voltages have been made. Like most other mercury lamps they will not light on alternating current. The ultra-violet light emitted is so intense as to colour glass globes a deep purple. The tubes in which the arc plays have normally an internal diameter of several millimetres.

If we regard the motion of the ends of the mercury columns in the necklace effect as being a simple harmonic motion, then, since experiment shows that the period varies as the square root of the length of the columns, we may regard the coefficient of the inertia term as being proportional to this length. The coefficient of damping due to the internal viscosity of the mercury will also be proportional to this length. The possibility of oscillatory motion depends on the relative magnitude of the square of the coefficient of damping and of the coefficient of inertia. So that, if the "Spring" be the same, then we can obtain a dead-beat motion by simply increasing the length without introducing any constriction into it.

Now the "Spring" is, as shown previously, largely settled by the external pressure. It is also affected by the mean current and arc length; but assuming that the "Spring" is chiefly decided by the pressure, then we can obtain a dead-beat motion by decreasing the pressure. These considerations suggest that increasing the length of the tube or decreasing the hydrostatic pressure should result in the formation of an arc of constant length. Both these conclusions are justified by experiment.

When the arc is of constant length, the effect observed in a rotating mirror is that of a ribbon of light. Fig. 14 (Pl. VI.) is the photograph of such a ribbon taken on a moving plate. The tube was of quartz (4 cm., 4.2 mm., .55 mm., 102 volts, 210 ohms), the current was .1 ampere and the volts across

the lamp 83. The pressure was 19.3 cm. of mercury. The current is flowing through the lamp from the lower (time signal) side to the upper side of the ribbon pattern. The surface of the cathode is seen to fluctuate rapidly in brightness as does the cathode in the necklace effect. These alterations show no regular periodicity. The vertical light and dark narrow bands represent irregular alterations in the brightness of the arc. They are apparently unconnected with the bright negative spots.

The alteration in the appearance of an arc which changes from a necklace to a ribbon is very marked even when viewed directly. If looked at through red glass, the whole ribbon is of uniform colour and brightness, but the waist of a necklace is much brighter than the rest and contains more orange light.

In the case of the arc of constant length, the luminous column generally moves slowly in the opposite direction to the current due to evaporation from the anode. Occasionally the ribbon effect continues for some time with great steadiness, then a flicker occurs which is followed by another period of steadiness. This flickering is met with in cases in which the progressive motion of the column of light in the direction opposite to that of the electric current is not noticeable. It is, in fact, due to an effect which is calculated to lessen or even to prevent the motion of the illuminated column of vapour. When such a lamp is examined with a magnifying glass through a suitable colour screen, the positive and negative ends appear quite different. Near the positive end over a distance extending a millimetre or so from the liquid mercury, the inner wall of the tube is seen to be covered by mercury dew. This increases in amount and the drops coalesce until a flicker occurs and the phenomena are repeated. No deposition can be seen in the rest of the space occupied by the vapour.

Where a lamp is giving the ribbon effect under higher voltages, it may go out from time to time and light up again automatically. The green glow proceeds from the ends of the vapour column while the main luminosity of the lamp is absent. This was well shown by a quartz tube (10 cm., 4.3 mm., .46 mm., 400 volts, 710 ohms) when the hydrostatic pressure was 29 cm. of mercury. The green glow also appeared when the current was switched off. If the current is turned on again while the glow is present, which may last several seconds, the lamp relights. This is so even when the direction of the current has been reversed.

The ribbon effect may sometimes be obtained by plunging



a lamp into a tank of cold water while it is giving the necklace effect. This experiment, of course, can only be tried with quartz tubing with any chance of continued success. If a lamp is running with a high resistance in series and giving a necklace effect, the ribbon is temporarily produced, in some lamps, by suddenly decreasing the resistance. When the ribbon breaks, it may give rise to the fan effect or to a broken necklace according as the tube is longer or shorter. With a tube which is known to give a good necklace with a certain voltage and resistance, it may, on first lighting up, give the ribbon instead, which becomes unstable as the tube gets hot. Or perhaps delay in assuming the necklace form may be a purely mechanical result consequent upon the oscillations requiring time for their amplitude to reach a steady value. An example of this was met with when performing experiments from which the lines AB and AC were drawn (Pl. VII. fig. 6), the following observations being taken with an electromotive force of 200 volts.

	External Resistance in ohms.	R.M.S. volts on lamp.	Current in amps.	Width of waist in cms.	Width of bead in cms.	Mean arc length in cms.	Drop of volts per cm. of mean arc length.
Necklace	1290	125	·07	·4	2·75	1·57	80
Limits .....	1820	88	·07	0	1·9	·95	93
Ribbon .....	1610	162	·025			1·25	130

The ribbon persisted for 23 minutes when it was replaced by the necklace arc, the current rising and the volts across the lamp falling. The rate of consumption of energy in the necklace effect is almost twice that of the ribbon effect for the same mean arc length. This suggests that an appreciable fraction of the electrical energy supplied to the necklace lamp is used in maintaining the oscillations of the viscous mercury.

With a fixed pressure, the external resistances on which a given tube will run as a ribbon lamp are confined to a region on a resistance-electromotive force diagram similar in shape to that found for a necklace lamp. On such a diagram (see fig. 15, Pl. VII.) there is an area ABA'C, indicating the ranges of volts and ohms within which the ribbon is produced. If a ribbon lamp is alight and the resistance is increased so that the tracing point crosses the line AB, the arc shortens and finally goes out on the contact of the mercury columns; meanwhile the volts across the lamp fall and the current

risers. If when the lamp is alight the resistance is reduced until we cross the line A'C, the arc lengthens and is extinguished. The volts on the lamp gradually rise during this increase in length and the current falls. The ribbon region bounded by the lines AB and A'C is comparable with the necklace region bounded by the lines AB and AC in fig. 2. In the case of the necklace above AB, each separate arc keeps alight until the mercury columns come together; below AC, each separate extinction occurs while the columns are still separated.

In the diagram fig. 15 which refers to a quartz tube (54 cm., 4.2 mm., .37 mm.) when the pressure was 80 cm. of mercury, it was found that the lines BA and CA' could not be experimentally produced towards A and A' because the lamp could not be lit on a voltage below 200. The boundaries of the ribbon region could probably be better determined by lighting the lamp on an electromotive force of say 200 volts, and then lowering the voltage gradually by the use of a suitable battery switch.

The ribbon region on a diagram such as fig. 15 is always bounded by two lines rising from left to right. The broken lines *ab*, *a'c* on the diagram are the boundaries of the ribbon region with 60 cm. pressure. With a fixed electromotive force and under constant pressure the root mean square volts across the lamp and the arc length decrease as the external resistance increases, while the current and the mean electric force in the arc are either constant or change very slightly compared with the changes in the arc length and difference of potential between the electrodes. A number of sets of experiments in which the pressure and the electromotive force were kept constant and the current, arc length, and volts across the arc were measured as the resistance was changed have been performed. Fig. 16 gives the result of one such series.

The current is generally nearly constant for each pressure but rises with increase in resistance for higher pressures. If the resistance is made the mean between the lowest and highest on which the arc is stable for any given electromotive force and pressure, then the current falls with rise of pressure, as below, for a fixed electromotive force of 400 volts.

The volts per cm. of arc length are nearly constant for any given pressure, but fall slightly for low pressures, and rise slightly for high pressures, as the resistance is increased. The volts per cm. of arc length corresponding to the mean

Pressure.	Current.	Volts per cm.	Volts per cm. sq. rt. of Press.
25	·035	66·5	13·3
30	·033	73	13·3
41	·031	84·5	13·2
60	·028	107·5	13·9
80	·028	122·5	13·8
100	·028	139·0	13·9

resistance, and therefore to the currents, are given in the above table. The mean electric force in the arc for a constant current is then directly as the square root of the pressure.

If the volts on the arc are plotted against the arc length for a given pressure, and for a fixed electromotive force, the result is a straight line. This line generally cuts the axis of volts above the origin, indicating the presence of an anode and cathode drop of potential of a few volts. If, however, the results are plotted for different electromotive forces, this effect is entirely masked and a straight line through the origin gives the relation between the difference of potential and arc length for any pressure. A diagram of this kind is given in fig. 17, in which the full lines show the range of each set of experiments at each pressure.

These lines could not be extended by experiment towards the origin, as the arc would not light on low voltages. This difficulty has already been mentioned in describing fig. 15.

The volts on the lamp for a given arc length can be read from fig. 17. Thus, for arc length 3 cm. we have :—

Pressure.	Volts on Lamp.	Volts Root Press.
25	197	39·4
30	218	40·5
41	254	39·7
60	318	42·6
80	379	42·4
100	417	41·7

which gives us that the mean electric force is approximately as the square root of the pressure for the same arc length.

## INTERMITTENT ELECTROMOTIVE FORCES.

If the secondary circuit of a small induction-coil is completed by means of a capillary tube containing mercury, and mounted as usual, very interesting effects are obtained if the middle of the tube is heated by some external source. If the tube is short, and the pressure approximately that due to the atmosphere, brilliant luminous effects are produced, which are seen in the revolving mirror to be of the necklace type, but marked by broad bands of darkness corresponding to the periods of little or no applied electromotive force. These bands may be made very thin by using a large current in the primary circuit. The outlines of the necklace at the ends of the dark transverse bands are often marked by bright points of light, which produce a most beautiful appearance when the bands are broad. Using a quartz tube (10.7 cm., 6 mm., .9 mm.) heated by a Bunsen flame, a brilliant intermittent arc 4 cm. long could be maintained as long as desired. The coil was a six-inch Apps coil with a two-volt accumulator on the primary.

Glass tubes can be used in this experiment, and will often last an hour or longer. This is a very simple way of getting mercury light for laboratory purposes.

Under reduced pressure, or by the use of a long capillary tube, the heat-supply serves to keep the column of mercury broken, and, as with the ribbon effect already dealt with, the mercury remains at rest in the tube. Using a small coil, as before, it is possible in this way to get a very bright mercury arc. In the revolving mirror the ribbon is seen to be crossed by a series of dark lines, as before.

## ALTERNATING ELECTROMOTIVE FORCES.

When alternating electromotive forces are employed, effects of the fan type are always produced unless heat is independently applied. Fig. 18 (Pl. VI.) is a photograph of the arc in a quartz tube (4 cm., 4.2 mm., .55 mm.). The electromotive force was 105 volts, and the frequency of the supply 61. The pressure was 80 cms. of mercury, and the resistance in series with the lamp 150 ohms. The frequency of the separate arcs is the same as the frequency of the supply; so that only half of each complete wave of electromotive force is concerned in the production of the luminosity.

If a moving-coil ammeter is inserted in the circuit, the current is found to be rectified; but the selective effect is variable, and the mean current changes in direction

arbitrarily at intervals. If a few accumulators are placed in the circuit, the change in direction still occurs; but if the cells are increased in number, a stage comes when the current is always in such a direction as to discharge the cells.

Experiments in which the applied alternating electromotive force was raised gradually to 1200 root mean square volts, and the resistance varied on each voltage, were carried out. No marked variation from the appearance as shown in fig. 18 was found on examining the arcs in the revolving mirror. The fraction of a period during which the arc persisted was slightly longer with higher voltages.

On supplying heat to the tube, and using high alternating electromotive forces, the appearance presented in the revolving mirror depends on the pressure and length of tube. With low pressures or long tubes, the heat produces a ribbon which is lit up by the current. The ribbon is crossed by equidistant dark narrow bands corresponding to the passage of the electromotive force through its zero values. If the tube-length and pressure be such as that the heat supplied gives a necklace motion to the column, then the appearance is that of a necklace lamp, the band of light being again crossed by black lines of no electromotive force. For these experiments a small induction-coil used as a high-tension transformer was found convenient. By heating the quartz tube in a Bunsen flame, a brilliant arc from 5 to 10 cm. long can be maintained as long as desired.

#### ELECTRICAL OSCILLATIONS.

The irregular vertical striæ already noted in the photograph of the ribbon (fig. 14, Pl. VI.) are replaced by uniformly spaced alternations of brightness when the lamp is run from a dynamo (fig. 19). These bands are due to the change in the electromotive force in the circuit consequent on the passage of the teeth of the armature past the poles of the dynamo. Similar effects are produced in the necklace pictures. In fig. 20 the only circumstances changed from those of fig. 1 are that now the current is derived from a dynamo (103 volts) and the resistance is 150 ohms. The alternations of brightness have a frequency of 640; this number was found to be nearly identical with the frequency of the replacement of one tooth of the armature by the next, as calculated from the speed of the dynamo determined as soon as possible after the photograph was taken.

Fig. 21 bears a strong likeness to fig. 19, but in this figure the lamp was operated from cells and not from a

dynamo. The striations are due to oscillations in a circuit consisting of the lamp with coils and condensers arranged in series, the coils and condensers being in parallel with the lamp. The experiment is a variation of those of Duddell on the singing arc. The calculated frequency of the oscillations in this circuit, neglecting resistance, was 950. The effective resistance of the arc was found to be 860 ohms, the other resistance in the oscillatory circuit being 120 ohms; allowing for this total resistance of 980 ohms, the corrected frequency becomes 864. By measuring the photograph, the observed frequency is 869.

Striations can also be obtained by similar methods when a lamp is giving the fan effect. Increasing the self-induction or the capacity lengthened the period.

Attempts to obtain photographs of a striated necklace by this method have been unsuccessful, the disturbance produced by the shunt-circuit being great enough to cause the necklace to break.

### THE GREEN GLOW.

This was first noticed in connexion with this research when experimenting on the ribbon effect. It was found that when the current was switched off while the lamp was giving a steady arc between the ends of the broken mercury columns, under reduced hydrostatic pressure, the light did not go out at once, but lingered feebly between the two columns. As the tube cools in a second or two, the columns have approached within a couple of millimetres or so, and then this glow dies out; the ends of the column then approach steadily until they join.

This light, when produced in fused quartz lamps from which the current has just been switched off, looks grass-green in colour, in contrast to the bluish-white light deficient in red to which the eye has just been exposed. In contrast, however, with daylight it is of a greenish-blue tint.

In most cases when the current is switched on again while the green glow continues, the lamp relights. Sometimes the main luminosity of the lamp when giving the ribbon effect on a high voltage (400) suddenly ceases. In short tubes the green glow then appears, and may be replaced as long as eight seconds later, by the lamp lighting again automatically, without the columns having come into contact.

The green glow is not caused by the external electromotive force applied to the tube, nor does it necessarily depend for its formation upon the vapour having previously been

conducting electricity. It usually owes its existence to the rapid movement of the mercury against the walls of the tube.

The phenomenon is the same as that occurring in an ordinary mercury still; it has been known since 1676 that the motion of mercury in an exhausted glass vessel gave rise to luminous effects, which since 1705 have been correctly regarded as of electrical origin. (Cajori, *History of Physics*, p. 96.)

It is not, however, generally known that the effect can readily be observed without the trouble of producing a vacuum space and by employing the automatic pulsations of mercury columns caused by heat. A quartz tube (10 cm., 4.3 mm., .46 mm.) was mounted between the glass bottles as usual. This tube was then used in a variety of experiments, and the mercury column always rapidly became continuous when the current was switched off; so that one may be certain that it contained little of anything but mercury. This tube was then placed so that its central portion could be conveniently heated by a Bunsen flame. The green glow soon made its appearance. The portion of the tube immediately above the burner appeared empty and gave out no light; but this region was followed on either side by about 2 cm. of space which glowed with the characteristic green light. While the glow is present, the vapour is in a highly-conducting state. A moving-coil milliammeter of four ohms resistance was put in circuit with the tube, a rheostat, and a large accumulator of 2 volts. When the column of mercury was continuous, the reading of the ammeter was 50 milliamperes. The resistance in series with the lamp was 37 ohms in all. On applying the flame, the current varied irregularly from 4 to 5 milliamperes. Thus the effective resistance of the space occupied chiefly by vapour was only about 400 ohms.

It is to be noted that the conductivity is a concomitant of the green glow. If the glow is absent and the columns of mercury are separated, the vapour is non-conducting when tested with low voltages. This matter was given particular attention in a further confirmatory experiment performed with a quartz tube (10.7 cm., 6 mm., .88 mm.). This was put into an electrical circuit, as above. When the Bunsen flame first caused the columns to separate, the current fell to zero. When the glow commenced, the current rose from 5 to 6 milliamperes. On removing the flame the glow continued for a short time, and so also did the current; then the glow and current ceased simultaneously. The ammeter continued to record zero until the columns joined.

It was found that the central portion of the tube was not

absolutely empty of liquid mercury. Very small drops could be seen to be present ; they were in rapid movement to and fro along the tube. In spite of this, it is probable that the electric current was carried almost entirely by the vapour, since these drops never became large enough or numerous enough to form a bridge between the ends of the columns. On repeating this experiment with the same tube, similar results were obtained, but the conductivity was even greater than before. Changing the direction of the applied electromotive force produced no apparent effect. By using a sheet-iron flame-shield for the Bunsen burner, it was found possible to so arrange the height and distance of the flame as to cause the green glow to be emitted for as long as one wished. In this case the tube was shorter, and a little water was put in the bottles to moderate the temperature of the mercury. Using a tube of quartz, mounted as usual (6.15 cm., 5.5 mm., .4 mm.), it was possible to so arrange the flame as to cause the green glow to be given out with great regularity for hours together.

When examined in a rotating mirror, the luminosity was seen to proceed from positions in the tube the distance apart of which varied in a periodic manner. The appearances showed that the motion of the columns of mercury were of the necklace type. In this case the heat necessary to maintain the oscillations is supplied by the Bunsen burner from without, and in the necklace effect the heat is supplied by the electric current from within. If one continues to observe the glow in the rotating mirror when the flame is turned out, it is seen that the luminosity does not cease at once, but its periodic character is lost very rapidly.

A very bright persistent green glow can be obtained by placing a Bunsen flame under the quartz tube and exhausting the air from one of the bottles when the mercury column has broken. The luminosity thus produced can be made several centimetres long, and will persist indefinitely. It is caused by the motion of the condensed drops of mercury as they pass towards the cool end of the vapour column. The visible spectrum of this glow shows the following lines :—

4047	Violet,
4358	Blue,
5461	Green,
5770	} Yellow,
5790	

together with a background of what appears, under the dispersion employed, to be a continuous spectrum extending



from between the violet and blue to beyond the green. When the pressure is allowed to rise to that of the atmosphere in both bottles, the glow gives a shorter continuous spectrum and the violet line 4047 is no longer visible.

Attempts to obtain the green glow in glass capillary tubes by heating have been unsuccessful.

#### PHOSPHORESCENCE OF FUSED QUARTZ.

A very interesting phenomenon exhibited by the quartz lamps described in this paper is the remarkably bright phosphorescence which is observed on switching off the current. The phosphorescent light is generally of a faint green tint, but one specimen gave a yellowish light. The light is often bright enough to be detected in a well-lighted laboratory, and in the dark may be visible for more than a minute after turning off the current. The quartz, after having lost its phosphorescence, may be made to glow again by heating. This heating will cause the renewal of the luminosity even after the quartz has been kept in the dark for several months.

This phosphorescence can be produced by exposing fused quartz to the light from any of the lamps described in this paper. Crystalline quartz does not exhibit this effect. The phosphorescence of fused quartz is not a noticeable feature of quartz vacuum lamps. This is probably owing to the intensity of the radiation in the particular region of the spectrum required to produce the phosphorescence being greater when the pressure of the mercury vapour is increased. Mr. H. G. Lacell informs me that he has noticed this phosphorescence in connexion with the lamp described at the beginning of the section on the ribbon effect.

#### CONCLUSION.

Many of the phenomena described in this paper require further study with the help of the spectrograph, the oscillograph, and the photometer. Much of the work should be capable of repetition, using conductors other than mercury.

The best thanks of the author are due to Professor Sir J. J. Thomson, F.R.S., for valuable advice during the progress of the work; to Mr. C. Dearing, B.Sc., for aid in some of the experiments; to Mr. S. Lawrance for assistance throughout the research; and to Mr. H. G. Lacell and the Silica Syndicate, who have kindly provided the quartz apparatus.

L.C.C. Paddington Technical Institute.

*Phil. Mag.* S. 6. Vol. 22. No. 130. Oct. 1911.

2 N

L. *Groove-Form and Energy Distribution of Diffraction Gratings.* By AUGUSTUS TROWBRIDGE, Ph.D., Professor of Physics, and IRVING B. CRANDALL, A.M., Scholar in Physics, Princeton University\*.

[Plates VIII.-XII]

CONTENTS.

- § 1. Introduction.
2. Method and arrangement of apparatus.
3. The concentration of energy in a single order.
4. Corrections to the curves.
5. The relation between the shape of the groove and the direction of concentration.
6. Weak orders; the retardation over a single element.
7. Conclusion.

§ 1.

IN a series of papers which have appeared in this Journal (vol. xx.), by R. W. Wood and one of the present authors, it has been shown that it is possible to construct diffraction-gratings suitable for use in the infra-red spectrum which concentrate the greater part of the energy into a single order, and that it is possible to predict where this concentration will occur from the shape of the groove which is ruled on the grating surface.

In the investigation described in one of the papers referred to above†, a study was made of four gratings with constants 0.0123 mm., and two with constants 0.0265 mm., all six ruled on gold with a carborundum crystal placed in various azimuths. The distribution of the energy among the various orders was obtained bolometrically for two relatively narrow regions in the infra-red spectrum of mean wave-lengths  $4.3\mu$  and  $8.6\mu$ . In the case of gratings of so large a constant the form of groove could be inferred from inspection with the microscope, and yet the ratio of grating space to wave-length of the incident energy is about that which obtains in practice with the usual grating in the visible spectrum; that is, the grating is about fifteen times as coarse as one suitable for optical work, but the length of wave is from ten to twenty times as great. In the investigation above referred to, the ratio between wave-length and grating space was greater than the value which limits the applicability of the simple diffraction theory, and as the results obtained were in fair qualitative agreement with theory it was thought advisable by the present writers to extend the research towards the visible spectrum.

\* Communicated by the Authors.

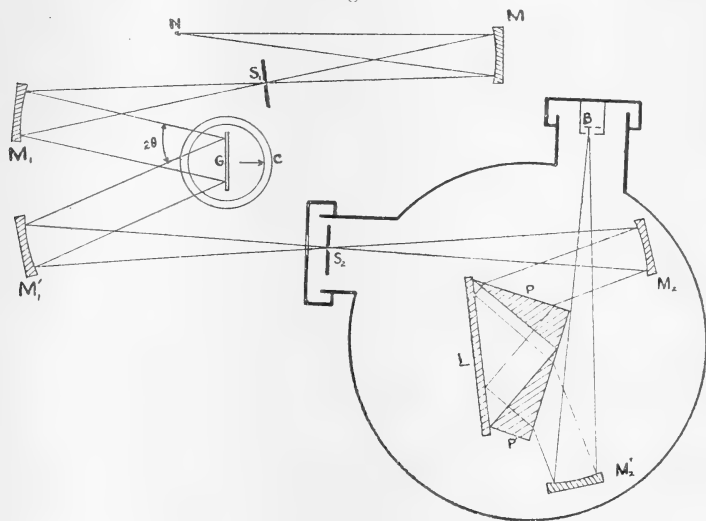
† Phil. Mag. [6] vol. xx. pp. 886-898 (1910).

The report of this work, the development of a simple formula adapted to the experimental conditions of the work, and an analysis of the results obtained with reference to the demands of this formula constitute the subject matter of this paper.

## § 2.

This investigation had for its object the systematic examination of the energy diffracted from some typical echelette gratings throughout a fairly large region of the infra-red ( $1-6\mu$ ); the determination of the shape of the groove of the gratings used, and, if possible, the discovery of the relation between the shape of the groove and the varying quantity of energy thrown off at the different angles. The gratings selected were two (Nos. 6 and 7) of the gratings ruled by R. W. Wood for the above mentioned work, and one ruled by Dr. C. F. Brackett (No. 10) with a diamond crystal ground so as to rule a groove with one vertical side, and one very gently sloping side. These three gratings combined a fairly high dispersion with a very small angle between the undisturbed surface and the main plane of the groove, these conditions being essential to the crowding of the energy into a single order; this order being as low as possible.

Fig. 1.



The essential parts of the apparatus were two spectrometers; referring to fig. 1, the grating G was mounted on the divided circle C of the first spectrometer: the light from the Nernst lamp N passing through the system by way of

mirror M, slit S<sub>1</sub>, mirrors M<sub>1</sub> and M<sub>1</sub>', so that the spectra from the grating fell on the slit of the second spectrometer at S<sub>2</sub>. The first spectrometer is thus arranged as an ordinary grating spectrometer with fixed angle between collimators. Successive orders on each side of the central image are brought onto the slit S<sub>2</sub> by rotating the grating through an angle  $\delta$  such that

$$n\lambda = 2b \cos \theta \sin \delta,$$

where  $2\theta$  is the angle between collimators and  $b$  the grating space.

For the second spectrometer the vacuum instrument designed by one of the present authors\* served to resolve the energy falling on the slit into the different components due to the overlapping of orders of the grating spectra. The two 30° rock-salt prisms P and P' together with the plane mirror L form a Wadsworth combination, which is equal in dispersive power to a 60° prism. The two mirrors M<sub>2</sub> and M<sub>2</sub>', placed so that the slit S<sub>2</sub> and the bolometer strip B are at their respective foci, complete the optical system of the second spectrometer. The bolometer strip B was exactly the width of the slit S<sub>2</sub>, namely about 0.7 mm., or about 3 minutes of arc in terms of the rotation of the prism system. The current through the strip was about 0.05 ampere, and the sensitiveness of the galvanometer was about  $5 \times 10^{-10}$  ampere per scale-division (millimetre), its resistance being 3 ohms.

In practice the vacuum spectrometer was set so that a particular wave-length interval fell on the strip B, and the grating C was turned through the series of angles: thus were obtained a series of deflexions which were proportional to the energy radiated from the Nernst lamp for this wave-length, and diffracted by the grating into the several orders of spectra. The observations for the three gratings are plotted in the curves which constitute the three accompanying Plates. The abscissas represent the angular readings of the grating spectrometer; the ordinates the corresponding deflexions in centimetres. There was also taken a series of observations to determine the energy radiated from the Nernst lamp, and undergoing reflexion from a gold mirror, as this is the kind of surface on which the gratings are ruled. In considering the curve obtained for a grating, using any particular wave-length, the relative quantity of energy available at this wave-length due to the above conditions must be kept in mind; also there may be noted absorption bands

\* A. Trowbridge, Phil. Mag. [6] vol. xx. p. 768 (1910).

at  $2.1\mu$ ,  $2.7\mu$ , and  $4.6\mu$ , due, respectively, to selective emission of the Nernst filament\* and to absorption by water-vapour and carbon dioxide in the air; these will of course appear in any readings which are taken at these wave-lengths, and have nothing to do with the properties of the gratings.

### § 3.

An inspection of the set of curves (Pls. VIII.-X.) obtained from any one of the three gratings will show the marked asymmetry of its spectra. A large portion of the energy appears concentrated in one order, or, under the worst conditions, in two neighbouring orders. The area under any part of the energy curve is proportional to the total energy thrown into that part of the spectrum. The total area, as well as that for the principal orders of concentration, was determined with the aid of a planimeter, and the percentage of the total energy which lay in this order was computed from these data. We shall select the Brackets grating No. 10 (Pl. X.) as the best example, since this combines the two qualities of resolution and concentration to the greatest degree. We append here a table of its properties:

Brackets Grating No. 10.

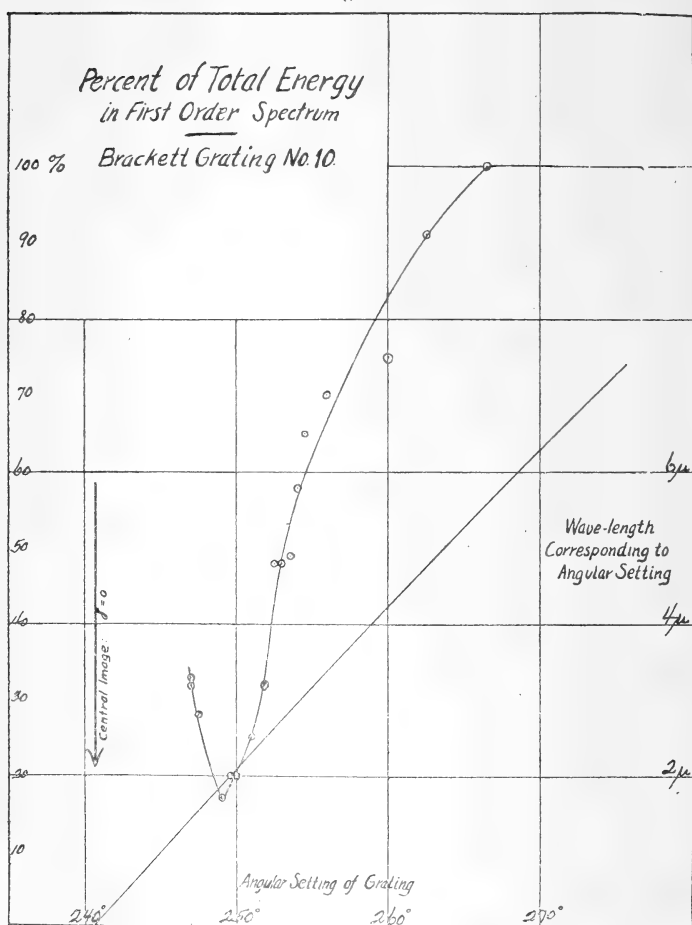
$\lambda$ .	Order in which energy is concentrated.			Percentage of energy in this order.		
$1.4\mu$ .....	1,	3,	4	32,	18,	25
$1.6$ .....	1,		3	33,	28	
$1.8$ .....	1,	2,	3	28,	$13\frac{1}{2}$ ,	33
$2.0$ .....		2			31	
$2.1$ .....		2			31	
$2.2$ .....		2			35	
$2.4$ .....	1,	2		25,	35	
$2.6$ .....	1,	2		32,	34	
$2.8$ .....	1				48	
$2.9$ .....	1				48	
$3.0$ .....	1				49	
$3.2$ .....	1				58	
$3.4$ .....	1				65	
$3.9$ .....	1				70	
$4.5$ .....	1				75	
$5.2$ .....	1				91	
$6.0$ .....	1				100	

Starting with the shorter wave-lengths, the energy is seen to lie principally in three orders, all on one side of the

\* W. W. Coblentz, Bull. Bureau of Standards, vol. iv. no. 4 (1908).

central image. The mean angle about which the energy is disposed is  $20^{\circ}$ – $25^{\circ}$  from the position of the central image. As the wave-length is increased, the orders move farther and farther out from the central image, consequently the energy becomes concentrated in lower orders during the process. Beginning with wave-length  $2.8\mu$  the first order

Fig. 2



predominates, and since there cannot be fractional orders of spectra, it is evident that more and more of the energy will be thrown into this order as the wave-length is increased, a conclusion which is wholly substantiated by the curves for greater wave-length. A curve is plotted (fig. 2) showing

the variation of the percentage of the energy in the first order with increasing wave-length. It will be noted that the curve goes through a minimum at wave-length  $2\mu$ . This is due either to the absorption band at  $2.1\mu$  affecting the first order rather more than either of the others, or, as is more likely, the order in this position is a weak order on account of a destructive diffraction due to the shape of the groove; this effect will be fully considered in § 6. As will be seen later, the shape of the groove is not accurately known for this grating, but it is evident that the distribution of the energy from it is what might be expected from a grating that would naturally reflect energy from one side of the groove in the direction  $20^{\circ}$ – $25^{\circ}$  out from the central image.

#### § 4.

The wave-lengths accompanying the various curves are only approximate, as there was a lost motion in the vacuum spectrometer which was not detected until the experimental work had been completed. This point is not vital, however, as the intention of the authors was not to make accurate wave-length determinations, but to take serial readings and determine the quantity of energy thrown off with the grating in the different positions.

By referring to the curve for the energy from the Nernst lamp after it has undergone reflexion from a gold mirror (fig. 3, p. 540), it will be seen that the maximum of the energy distribution for a given wave-length will be shifted in angular reading if the wave-length correspond to a point on either of the steep portions of the curve. Paschen\* has worked out this correction, and it was applied to the curves of the Wood grating No. 7. The true location of the maximum is shown by the dotted curve slightly displaced from the observed maximum, this displacement being to greater or less wave-length, according as

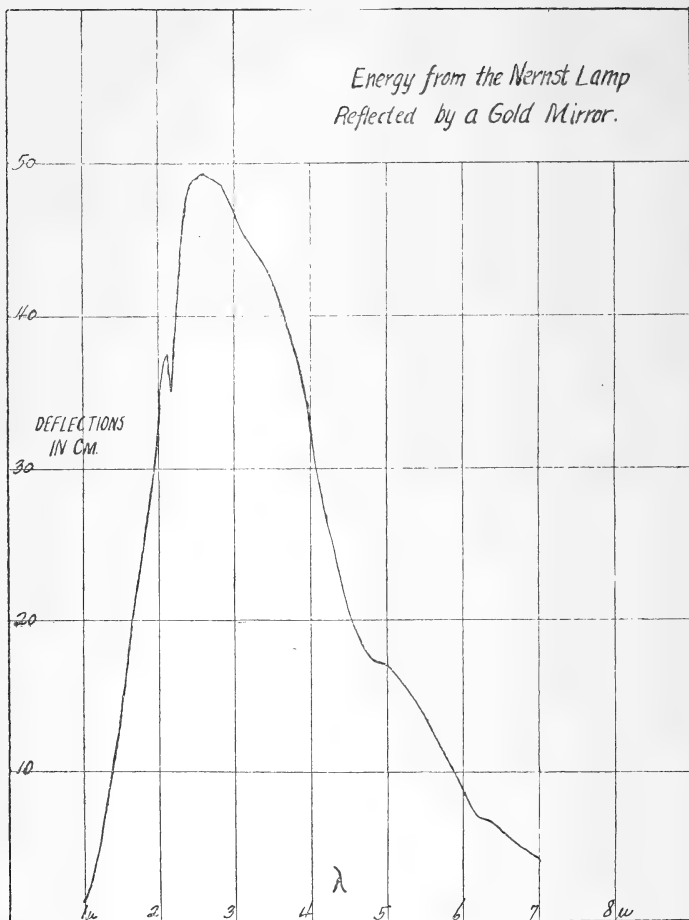
$$\lambda > 2.6\mu \quad \text{or} \quad \lambda < 2.6\mu.$$

This correction is of importance only in one respect: it enables the exact wave-length to be calculated from the true position of the maximum of a given order and the constant of the grating; this accurate value of the wave-length is essential when the questions of retardation over a single

\* *Wied. Ann.* vol. li, p. 8 (1894).

540 Prof. Trowbridge and Mr. Crandall on *Groove-Form* element, absent orders, &c., are considered, as will be seen later\*.

Fig. 3.



\* There is a further correction, due to the fact that with a setting of the grating so that orders to one side of the central image are on the slit of the vacuum spectrometer, the dispersions of grating and prism are additive, while with orders on the other side of the central image, the dispersions oppose one another. Thus of two equal maxima, one on each side of the central image, one would appear more spread out than the other, if this effect were noticeable; however, this correction was worked out from the dimensions of the slit, dispersion of the grating and rock-salt prisms, and found to be vanishingly small ( $< .001\mu$ ) in comparison with either of the two above mentioned corrections, and therefore negligible in this work.



§ 5.

There are several methods of determining the shape of the groove in the gratings employed. If the main plane of the groove be a perfectly plane mirror the grating, mounted in a system with fixed collimators, may be turned through the angle between the principal plane of the groove and the undisturbed surface; this will bring an image reflected from the plane of the groove into the observing telescope, and the angle is easily read. This image may be designated as the "oblique" image. However, if the surface of the groove is a poor reflector for light the definition is liable to be so bad that the above described method will not give consistent results. In place of the observing telescope a direct-vision spectroscope may be used, and the position of the oblique image determined by setting so that the brightest and most complete spectrum is seen; this of course postulates a similar behaviour of the grating in the visible region of the spectrum to that observed in the infra-red. A third method consists in making a replica from the grating, using collodion stained with a very dark colour; these replicas are embedded in a block of wax and sectioned through, in planes at right angles to the direction of the grooves, by a microtome. These sections may be mounted on slides, and the shape of the groove may be determined visually with a microscope, or from a microphotograph of the section.

Optically, all the gratings used gave very unsatisfactory definition of the oblique image; the replica process was resorted to in order to find out approximately the shape of the grooves\*. This brought out the fact that all the gratings with the exception of the Wood No. 7 had grooves the sides of whose profile were irregularly curved, but the Wood grating No. 7 showed as a groove profile a triangular shape: the sides of this triangle being fairly straight lines. Since this grating gives the simplest form of groove, it will be used in all calculations in which the geometrical properties of the groove are involved. Unfortunately, due to the shrinkage of the collodion film, and the fact that the section was not taken exactly perpendicular to the direction of the groove, the value of the angle taken from the microphotograph may not be relied upon; however, the ratio of the projections of the two slanting sides of the groove upon the undisturbed surface is a constant quantity, independent of the angle at which the section is taken:

\* The authors are indebted to Prof. C. F. W. McClure and Mr. Otto Kampmeier, of the department of Biology of the University, for taking and mounting the sections and making microphotographs.



Plate for No. 7, Pl. ~~IX~~.) There is almost no central image with the grating No 7, so we are justified in assuming that there remains none of the original surface, *i.e.* the grooves

join on, point to point. This establishes the ratio  $\frac{c}{b}$ , and  $c$  may

be computed, as  $b$  is known, being the value of one space of the grating. Since the true value of the angle  $A$  is not necessarily  $19^\circ$  the grating was mounted in the fixed collimator apparatus with the direct-vision spectroscope, and using this method the angle was found to be about  $23^\circ$ . As confirming this result, reference to the curve for wave-length  $4.65 \mu$  for this grating will show that when the second order is located about  $23^\circ$  out from the central image, the orders on either side of this order are most symmetrically arranged. Neither of the two observations are sufficient alone, but agreeing as they do, we are justified in taking the angle as  $23^\circ$  approximately. All the elements of the groove are now known and are given in fig. 4 *b*.

The series of observations for both the Wood grating No. 7 and the Brackett grating No. 10 show conclusively that the assumption by Messrs. Wood and Trowbridge that the energy diffracted appears in the direction in which it would naturally be reflected is completely justified. There remains, however, the consideration of the weak orders, which are particularly noticeable in the curves for the Wood grating No. 7.

## § 6.

It is well known that with an ordinary grating in which the element is composed of equal reflecting and non-reflecting parts, the even orders are missing, due to the fact that in the position where these orders would naturally occur, the retardation over the reflecting portion of the element is such that the effect from each element destroys itself, according to the elementary theory of diffraction from a slit. The curves for the Wood grating No. 7 show quite a number of instances of weak orders, and we now propose to consider this phase of the subject.

The form of the groove for this grating was established in § 5 (fig. 4 *b*). It will be seen from this that the narrow, steep plane of the groove is not in such a position that it reflects very much energy for the angular settings at which the grating is used. Further, it is not placed so that it cuts off any energy reflected or diffracted from the main plane of the groove. An expression very nearly rigorous for the retardation over the whole element may be found by

considering only that part of the wave-front diffracted from the portion AC of the groove. Referring to fig. 4 c :

$2\theta$  is the angle between collimators,

AA' is the oncoming wave-front,

AD is the diffracted wave-front,

$i$  is the angle of incidence,

$\theta - i = \delta$  is the angle of deviation of the grating from the position of the central image.

The retardation of the one end of the wave-front over the other is seen to be

$$\rho = AC(\cos A'CA + \cos DCA),$$

since

$$\cos A'CA = \cos \{90^\circ - (i + 23^\circ)\} = \sin (i + 23^\circ),$$

and

$$\begin{aligned} \cos DCA &= \cos \{2\theta + \angle A'CA\} = \cos \{90 - (i + 23^\circ + 2\theta)\} \\ &= \sin (i + 23^\circ - 2\theta), \end{aligned}$$

$$\begin{aligned} \rho &= AC\{\sin (i + 23^\circ) + \sin (i + 23^\circ - 2\theta)\} \\ &= 2AC \sin (i + 23^\circ - \theta) \cos \theta, \end{aligned}$$

or, since  $\theta - i = \delta$ , we have

$$\rho = 2AC \sin (23^\circ - \delta) \cos \theta^*.$$

The value of AB is  $\cdot 00123$  cm., the ratio  $\frac{c}{b} = \cdot 802$ , so that

$$2AC = \frac{\cdot 00123 \times \cdot 802 \times 2}{\cos 23^\circ} = \cdot 002136 \text{ cm.},$$

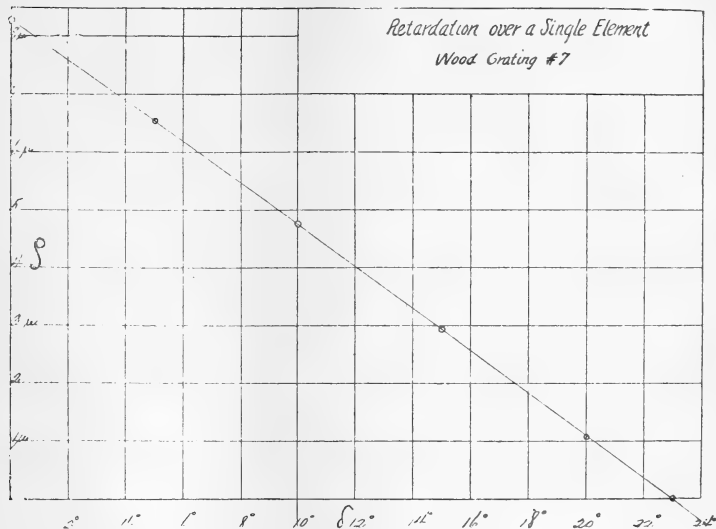
while the half angle between collimators is  $9^\circ \cdot 6$ . The curve showing the relation between  $\rho$  and  $\delta$  is given in fig. 5. Obviously the retardation must vanish when  $\delta = 23^\circ$ , *i. e.*, when the grating is turned so that the oblique image is viewed by the collimator. The retardation for any position of the grating may now be read off the curve, and if this were an exact multiple of the wave-length diffracted into the collimator for this setting, we should expect the order naturally occurring at this point to be extinguished. However, due to the assumptions made, and the fact that the plane AC is not a good enough mirror to define the oblique

\* If the side BC were vertical, it would, under some settings of the grating, cut off a portion of the diffracted wave-front so that a varying portion of the line AC must be used in deriving the formula. This is taken into account in the more general formula, since  $b=c$  in this case

$$\rho = 2b \cos \theta \sin (23^\circ - \delta) \frac{\cos(\theta + \delta)}{\cos(\theta + \delta - 23^\circ)},$$

image, total agreement between this theory and the observed phenomena is not reasonably to be expected; but in every

Fig. 5.



case where the effect is at all marked, the agreement is fairly good, as will be seen in the following table :

Wood Grating No. 7.

$\lambda$ .	Order in which energy is concentrated.	Percentage of the energy in this order.	Weak orders.	Retardation over the element.	Retardation in terms of wave-length.
1.16	9	57	5, 7	$3.4 \mu, 1.2 \mu$	$2.93 \lambda, 1.03$
1.47	7	60	3, 5	$4.6 \mu, 1.9 \mu$	$3.13, 1.29$
1.71	6	64	2, 5	$5.5 \mu, 1.8 \mu$	$3.21, 1.05$
About 2.30	5	68	4	$2.2 \mu$	1.10
" 2.30	4 & 5	together 71	1, 3	$6.55 \mu, 2.4 \mu$	$2.84, 1.04$
" 2.60	4 & 5	" 74	3	$2.5 \mu$	0.96
" 2.90	4 & 5	" 79	2	$3.35 \mu$	1.15
" 3.20	3 & 4	" 81	1, 2	$5.8 \mu, 3.3 \mu$	$1.81, 1.03$
" 3.50	3	77			
" 4.10	2, 3	40, 53			
4.65	2	75			
5.60	2, 1	60, 30			

Columns 4 and 5 show corresponding orders and retardations. The numbers in column 5 are almost exact multiples of the corresponding wave-lengths, as is shown in column 6,

This phenomenon will have to be taken into account as one of the properties of an echelette grating with a large, gently sloping surface as one portion of the element, and mounted in this type of spectrometer, *i. e.* with fixed collimators.

Some light may be thrown on the results found by Trowbridge and Wood\* with this grating, No. 7. It will be noticed that for wave-length  $4.3\mu$  the second order is strong (coming nearly at the angle  $23^\circ$ ), while the first and third orders are very weak. The retardation over the element for the first order is  $4.39\mu$  or almost exactly one wave-length. The retardation for the third order (situated  $33^\circ$  from the central image) may be found by producing the curve beyond the point  $23^\circ$  and will be a like amount. Thus the absence of these two orders agrees with the theory. On the other hand the small amount of energy in the first order for wave-length  $8.65\mu$ , coming at the concentration point, is not at all accounted for. However, it will be noticed that even this small amount of energy is all there is for the whole grating (with the exception of the central image), and it is probable that something happened after the observations for No. 6 were taken, but before those of No. 7 were taken, so that the total energy striking the grating was diminished.

It must be remarked that, since the energy absent from the weak orders is not destroyed, it must be sent into a neighbouring order, and this may either help or hinder the concentration of energy in a particular region in which it may be desired to use the grating. The case of Trowbridge and Wood's observations on No. 7 for wave-length  $4.3\mu$  is an admirable illustration of the building up of an order at the expense of two neighbouring orders, due to this effect. The retardation over the element at  $\delta=0$ , the position of the central image, is about *two* wave-lengths, and this, by reducing the central image, contributes further to the strengthening of the second order. To fully describe the grating No. 7, it would be sufficient to state that it is excellent for work in the region  $4\mu < \lambda < 5\mu$ .

### § 7.

We have seen that the energy is, in general, thrown out principally at the angle at which it would naturally be reflected, and that there is an effect due to the diffraction of the energy by the single elements. These two properties are not at all independent; for there can be no energy reflected from a surface in a direction such that the retardation over the surface gives rise to a destructive diffraction.

\* Phil. Mag. [6] vol. xx. pp. 886-898 (1910).

Consider the similarity between the general equation for the grating

$$n\lambda = 2b \cos \theta \sin \delta$$

(in which  $b$  is the grating space,  $2\theta$  the angle between collimators, and  $\delta$  the angular deviation from the position of the central image), and the equation for the retardation

$$\rho = 2d \cos \theta \sin (23^\circ - \delta).$$

If  $d$  were equal to  $b$ , as is approximately the case, the equations would be identical, if  $\delta$  were reckoned from the point  $23^\circ$  out from the central image, instead of directly from the central image. We may now say that an echelette grating, in which these two effects are combined, behaves from the standpoint of the distribution of the energy in every respect similarly to the ordinary grating; the difference being that, whereas in the grating the energy in the various spectra on either side of the central image falls off in certain ratios, in the echelette grating the point of reference is the oblique image, and the same ratios should hold for the energy in the spectra symmetrically disposed about the oblique image. The absent orders in the echelette spectra are exactly paralleled by the absent orders with a flat grating, any arbitrary portion of whose element is reflecting: the remainder throwing off no energy.

The arrangement of the fixed collimators was adopted by the authors as the most logical one, and this is always the easiest way to mount the grating for use in the infra-red spectrum.

To carry this work still farther, and make it productive of still more practical results, this type of grating should be thoroughly investigated in the visible region of the spectrum; it is the intention of the authors to do this as soon as gratings good enough for use in this region can be obtained.

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## LI. *On the Question of Valency in Gaseous Ionization.*

*To the Editors of the Philosophical Magazine.*

DEAR SIRS,—

IN a paper entitled as above, Millikan and Fletcher \* have come to the conclusion that when a gas is being ionized by means of radium or Röntgen rays, never more than one electron is driven away from the molecule, so that there

\* R. A. Millikan and Harvey Fletcher, *Phil. Mag.* [6] vol. xxi. p. 753 (1911).

appear only ions with either one positive or one negative charge. This result is contrary to measurements of Townsend\*, who found doubly-charged positive ions in the ionization by Röntgen rays, and contrary also to the conclusions which we† drew from the study of the velocity and the diffusion of ions, which were also generated by Röntgen rays. We have found that about 9 per cent. of the positive ions had a smaller (not more than half as great) coefficient of diffusion than the rest, and concluded from this that there existed 9 per cent. doubly-charged positive ions in this special case.

Millikan and Fletcher suppose that our result is caused by slow, so-called intermediate or Langevin ions, whose existence in this case, according to Pollock‡, is not wholly impossible. We have also thought of this explanation, but refused it, as apparently only slow positive ions were generated and there was no evidence why, if they were Langevin ions, that negative Langevin ions should not also exist, as in all other cases where these ions appear.

Now there can be no doubt but that the experimental device of Millikan and Fletcher appears superior to our more indirect method, especially as it gives the possibility of making the charge on individual ions subject to investigation. Nevertheless we are not able to consent to the conclusion of the authors as to the non-existence of the doubly-charged ions in the ionization by Röntgen rays, and we are rather inclined to believe that the conditions for their generation are not yet sufficiently cleared up. We want in the following to state some points which seem to favour our view.

It seems especially important to point to the fact that in the oil-drop method the observed number of doubly-charged ions does not directly give the amount per cent. of the same. Even if we put aside the violent recombination of this type of ions (that effect, in the case of Millikan and Fletcher, probably being small), there is still this to be considered—i. e., that the coefficient of diffusion of the doubly and more highly charged ions is far smaller than that of the univalent ones. And the influence of the diffusion on the probability for the oil-drop to catch an ion follows, even from Millikan's own paper on the elementary

\* J. S. Townsend, Proc. Roy. Soc. A, vol. lxxx. p. 207 (1908).

† J. Franck and W. Westphal, *Verh. d. D. Phys. Ges.* vol. xi. p. 146 (1909).

‡ J. A. Pollock, *Science*, vol. xxxix. p. 919 (1909).



charge\*. In this paper it is shown that an oil-drop, even when it already carries many negative charges, and therefore repels negative ions, nevertheless more frequently takes up negative than positive charges. This is the more striking, since in a condenser, whether it be charged or not, the number of the negative ions is smaller than that of the positive, which is due to the greater coefficient of diffusion and velocity of the negative ions. Even the increased frequency of "catches" of negative ions is to be explained by their greater diffusion; for, according to Ebert†, this adsorption of the ions is proportional to diffusion and velocity. Thus, with an equal number of ions of both signs, the ratio of "catches" for negative and positive ions should be 1.36. The ratio of diffusion of the doubly-charged ions to that of the singly-charged ones is 2; with those trebly-charged, a ratio of 3 is to be expected; and so on. Thus, due to the diffusion only, the observed number of doubly-charged ions must be multiplied by 2; and so on for the higher-charged ions. And this result would be the same, even if the diffusion of the multiply charged ions were the same as that of the single ones, because then the velocity of the variously charged ions would increase by the factors 2 and 3, and so on, so that the number of the corresponding ions in the gas would become smaller in the same ratio. Now let us consider Table III. in the paper of Millikan and Fletcher. We take this table, since it is only in this series that there are any observations which may possibly refer to doubly-charged ions. This possibility is even expressed by the authors themselves, but given up in favour of another explanation. In 79 cases which were observed, 76 showed a single charge, 3 a multiple charge. Of the latter, 2 are marked out as dubious. We may, however, take 2 of these observed 3 cases as real. If we take into account the diffusion, these 2 cases indicate at least 5 per cent. of the ions to be multiply-charged if there were only doubly-charged ions, and even more if there should be greater charges. Especially is this true if we consider that the multiply-charged ones are repelled much more violently from the positive oil-drop than the single ones. All these modifications of the ionic constants, the increased recombination, and especially the smaller diffusion and the increased repulsion from the drop, work together so as to cause the double charges to appear rarer than they really are. Indeed,

\* R. A. Millikan, *Phil. Mag.* [6] vol. xix. p. 209 (1910).

† H. Ebert, *Jahrb. d. Rad. u. Elektr.* vol. iii. p. 61 (1906).

they may altogether make the number appear several times too small.

Nevertheless, it may certainly be said that in the experiments of Millikan and Fletcher only very few doubly-charged ions existed. As this result differs, at least quantitatively, from ours, and ours again from Townsend's, the conclusion seems justified that the conditions for the generation of plurivalent ions are not yet sufficiently known. To throw some more light on them, we think it necessary to vary the experimental conditions widely. One of the points to be considered, as has been shown by Townsend, is the secondary radiator. In our experiments a secondary radiation may have come from lead, wood, aluminium, brass, or paraffin. This may explain the discrepancy between Townsend's and our experiments. It is not at all impossible that it may be necessary to use a homogeneous radiation of distinct frequency, such as is, according to Barkla and Sadler, originated in the secondary and tertiary Röntgen radiation. It may have happened that such a radiation has been generated in different amounts in the experiments of the different authors. Even the secondary cathode radiation may prove itself important. We want also to point to the fact that certain impurities in the gas, such as ozone or nitric oxides or other electronegative substances, seem to facilitate the detachment of an electron from a molecule, as is shown by some experiments now being carried on by one of us.

Finally, we want also to express the opinion that the results of Millikan and Fletcher still leave the question an open one, the more so since in other parts of physics observations of multiply-charged positive ions are actually beginning to accumulate. Thus the double charge of  $\alpha$  particles is now beyond any doubt: Gehrcke and Reichenheim\* have measured double charges in the anode rays of strontium; and in the Kanalstrahlen, J. J. Thomson†, v. Dechend & Hammer‡, and others have observed various atoms and molecules with multiple charges. For example, J. J. Thomson observed  $C_{++}$ ,  $C_{+++}$ ,  $N_{++}$ ,  $He_{++}$ ,  $Hg_{++}$ , and  $Hg_{+++}$ . There is evidently no relation to valency. Also, in these cases impurities seem to be important, as will be shown soon by one of us. Farther, we have no reason to assume that there should be any great difference between the ionization in an

\* E. Gehrcke and O. Reichenheim, *Verh. d. D. Phys. Ges.* vol. ix. p. 373 (1907).

† J. J. Thomson, *Jahrb. d. Rad. u. Elektr.* vol. viii. p. 2 (1911).

‡ v. Dechend and Hammer, *Jahrb. d. Rad. u. Elektr.* vol. viii. p. 1 (1911).

electric field and that by a foreign ionizing agent, especially as some properties of the gaseous ions (*e. g.*, the formation of clusters) have also been found in the Kanalstrahlen.

Thus we are inclined to believe that, under the right conditions, multiply-charged positive ions may be generated not only by Röntgen rays but also by any other ionizer.

Having just written this paper, we see in the last number of your Magazine a paper by J. S. Townsend on the same subject. We cannot but say that his views are in perfect accordance with ours.

Yours truly,

J. FRANCK and W. WESTPHAL.

Berlin,

Physikalisches Institut der Universität,

July 1911.

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LII. *On the Number of Ions produced by the Beta Rays and by the Gamma Rays from Radium C.* By A. S. EVE, M.A., D.Sc., McGill University, Montreal\*.

IN a previous paper †, an account has been given of the determination of the coefficient of absorption by air of the  $\beta$  rays from radium C, and a mean value  $\mu = 0.004 \text{ cm.}^{-1}$  was obtained, suggesting an average path of the  $\beta$  rays of 2.5 metres in air at atmospheric pressure ‡. This led to an estimate of the coefficient of absorption of the  $\gamma$  rays in air,  $\mu' = 0.000032 \text{ cm.}^{-1}$ , somewhat lower than that given by the ratio  $\mu'/D = 0.034$  of McClelland, whence  $\mu' = 0.000044$ , and yet smaller than the value derived from  $\mu'/D = 0.04$ , found by Soddy and Russell. In the work that follows, the intermediate value  $\mu' = 0.000044$  has been adopted. The value for  $e$ , the electronic charge, has been taken as  $4.9 \times 10^{-10}$  electrostatic unit.

In the present paper, experiments are described which lead to the evaluation of the total number of ions produced by the  $\beta$  rays, and of those produced by the  $\gamma$  rays, from one curie of radium C; that is, the amount of radium C in equilibrium with one gramme of radium. The heating effects of the  $\beta$  and  $\gamma$  rays may thus be calculated, and also the average number of ions produced by one  $\beta$  particle, both for its average path, and for 1 cm. of path. Corresponding

\* Communicated by the Author.

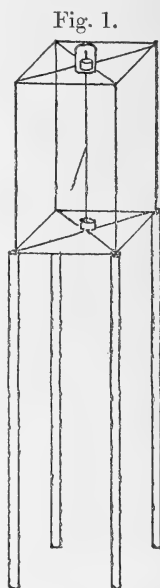
† Phil. Mag. July 1911.

‡ At short ranges with the active deposit of radium on aluminium foil I have recently found  $\mu = 0.012 \text{ cm.}^{-1}$ . In this case RaB was also sending  $\beta$  rays to the electroscope.

552 Dr. A. S. Evé on the Number of Ions produced by numbers, necessarily speculative in their values, have been estimated for the  $\gamma$  rays.

### *Electroscope.*

The electroscope was formed of a light framework of knitting-needles, standing on wooden posts (fig. 1). The framework was covered with aluminium leaf,  $\cdot 003$  cm. thick, offering a slight resistance to the  $\beta$  particle, not exceeding that of a cm. of air. The internal measurements were  $22 \times 11.5 \times 11.5 = 2910$  cm.<sup>3</sup> The central axis and aluminium leaf were insulated by amber beads, above and below, and the axis passed through the upper bead into the air for a distance of 7 mm., and this exposed end was covered with an ordinary thimble, which could be removed temporarily for charging. The usual charging-key was thus unnecessary—a great advantage when determining the capacity. One division of the microscope scale corresponded to 2.65 volts.



### *Capacity.*

It is difficult to determine with accuracy a small capacity, such as 2 or 3 cm. A method is given by Harms in the *Phys. Zeit.* (Jan. 15, 1904), and another by Campbell (*Phil. Mag.* Jan. 1911), but these involve, to some extent, connecting wires.

I have found it possible to obtain the capacity by taking straight thin wires, of length  $l$  and radius  $r$ , the capacities of which, away from conductors, are given by

$$\frac{l}{2 \log_e \frac{l}{r}}.$$

Two such wires, each of length 20 cm., having separately a capacity of 1.82, when placed end to end, together have a capacity of 3.21. When placing a vertical wire of length 20 cm. in contact with the axis of the electroscope, it was regarded as approximately one-half of a wire of 40 cm. length. There are further corrections, such as that due to the approach of the wire to the earth-connected upper plane

of the electroscope. Wires of 20, 30, 40, 50, and 60 cm. were used, of diameter .08 cm., and a similar series of diameter .048 cm. The electroscope, of unknown capacity  $C$ , had its vertical system charged to potential  $V$ , and when the insulated vertical wire touched it, the potential fell to  $V'$ . Thus

$$CV = (C + C' + x)V',$$

where  $C'$  is the capacity of the wire found by calculation (as for half a wire of double length), and where  $x$  is a small correction, apparently varying, approximately, inversely as the length. A large number of simultaneous equations were determined from the experiments, and these were plotted and solved graphically. A further check on the result was obtained by bringing up to the top end of a wire, when in contact with the central axis, spheres of known radii. The value of the capacity was found to be 2.90 cm., with a possible error of about 2 per cent.

#### *Measurements.*

Using the well-known relation

$$qSe = CV/300t^*,$$

it follows that  $q = 292$  divisions/minutes, where  $q$  is the number of ions per cm.<sup>3</sup> per second in the electroscope corresponding to a given leaf-measurement in divisions a minute.

If a quantity of radium  $Q$  is placed at a distance  $r$  from the electroscope,

$$q = K' \frac{Q}{r^2} e^{-\mu' r},$$

where  $q$  is the number of ions produced per cm.<sup>3</sup> per second by the  $\gamma$  rays from the radium  $C$  in equilibrium with the radium. When  $r$  is only 2 or 3 metres, we may omit  $e^{-\mu' r}$ , because  $\mu'$  is so small.

In order to find the constant  $K'$ , specimens of radium of strengths .23, .52, 1.6, and 8.5 mg. were used. A specimen was placed at distances varying from 75 to 300 cm., and was closely surrounded by cylinders of zinc or lead, between the poles of a large electromagnet. In this way the  $\beta$  rays were absorbed and deflected, but the correction for the absorption of the  $\gamma$  rays was as small as possible. The strengths of the radium specimens were determined by comparison with a

\* Rutherford's 'Radioactivity,' p. 87.

Rutherford & Boltwood standard at McGill University, and with another standard which was tested at Manchester University by the kindness of Professor Rutherford.

The mean result thus obtained was  $K' = 3.74 \times 10^9$ , with a possible error of about 5 per cent. Thus the number of ions produced by the  $\gamma$  rays from 1 curie of radium C at 1 metre from the source in air, at atmospheric pressure, is  $3.74 \times 10^5$  per  $\text{cm}^3$  per second\*.

In the Phil. Mag. Sept. 1906, is an account of a previous determination of this constant, and the value for  $K'$  then found with an aluminium testing vessel, for pure radium bromide, with  $e = 3.4 \times 10^{10}$ , was  $3.1 \times 10^9$ . This gives for radium, with  $e = 4.9 \times 10^{10}$ ,  $K' = 3.68 \times 10^9$ . This is 2 per cent. less than the present determination. I have placed aluminium cylinders about 1 mm. thick over the electroscope used in the experiments now described, and find that with  $\gamma$  rays alone there is an increase of about 5 per cent. in the ionization in the electroscope due to the surrounding aluminium cylinder, provided  $\beta$  rays are not coming from the source. The agreement between the old and new determinations is not, therefore, so good as at first appears. The former work, however, involved the very uncertain correction for a considerable absorption by lead, an error which has been now obviated.

The total number of ions per second due to  $Q$  curie of radium C is, therefore, in air

$$\int_0^\infty 4\pi r^2 dr K' \frac{Q}{r^2} e^{-\mu' r} = \frac{4\pi K' Q}{\mu'}.$$

On putting  $Q=1$ , it follows that  $N'$ , the total number of ions per second produced in air by the  $\gamma$  rays from one curie of radium C, is

$$N' = 4\pi \times 3.74 \times 10^9 / 0.00044 = 1.06 \times 10^{15} \quad . \quad (2)$$

Owing to uncertainty in the value of  $\mu'$ , this may have an error as large as 30 per cent.

In the work described above, the method of determining the capacity appeared open to criticism, although I believe that errors were eliminated in consequence of the number and variety of wires and spheres employed in the determination.

Professor H. A. Wilson suggested to me the use of an

\* In a paper to the Phil. Mag. Jan. 1911, I took  $K' = 3.1 \times 10^9$  instead of  $3.74 \times 10^9$ . All the results referring to  $\gamma$  rays in that paper require multiplication by 1.2.



556 Dr. A. S. Eve on the Number of Ions produced by every other part of the apparatus was earthed. The charge on the central wire and disk was, therefore,  $\frac{\pi r^2}{4\pi d} V$ , where  $r$  is the radius of the disk, and  $d$  its distance from the lowest plate. The disk and wire were then insulated, and all parts of the apparatus earthed. The charge on the central system and disk was now  $CV'$ , where  $C$  is the capacity to be determined and  $V'$  the potential found by the position of the gold-leaf and from the calibration curve. In the apparatus employed  $r=5.4$  cm.,  $d=1.5$  cm.,  $V/V'=3.25$ , whence  $C=15.8$ .

At 91 cm. the  $\gamma$  rays from 8.6 mg. Ra caused an ionization current of 13.5 volts/min., and as the volume of the electro-scope was 6100 cm.,  $q=3960$ . In this part of the experiment, it is necessary to surround the two lower aluminium plates with a collar of thin mica, shown in the figure. Therefore

$$3960 = K' \times .0085/91^2,$$

so that

$$K' = 3.81 \times 10^9.$$

This is about 2 per cent. greater than my previous value,  $3.74 \times 10^9$ . Although the capacity is determined more accurately with the guard-ring and disk electro-scope, it probably yields too large a value of  $K'$ , owing to some secondary radiation from the aluminium plates. The results, gave, therefore, a satisfactory verification of the first set of determinations.

#### *Number of Ions due to $\beta$ rays.*

When an attempt is made to determine the values of quantities corresponding to  $K'$  and  $N'$ , but relating to  $\beta$  rays instead of  $\gamma$  rays, difficulties occur. If the radium is placed in a receptacle, the walls absorb some of the  $\beta$  rays, and if the radium is placed on a plate, there is "reflected" radiation from the plate. The method employed to overcome these difficulties was as follows:—

The number of ions per cm.<sup>3</sup> per second, produced by the  $\beta$  rays from  $Q$  curies of radium  $C$ , at a distance  $r$ , is given by

$$q = K \frac{Q}{r^2} e^{-\mu r},$$

where  $K$  is the constant for  $\beta$  rays and  $\mu$  is the coefficient of absorption by air of the  $\beta$  rays.



At the same distance, with the same amount of radium C, we have

$$q' = K' \frac{Q}{r^2} e^{-\mu' r},$$

using accented letters throughout for  $\gamma$  rays, and unaccented for  $\beta$  rays.

By division,  $q/q' = K/K' \cdot e^{-\mu''}$ , and as  $K'$  has been found, suitable experiments determine  $K$ .

1. A capsule, containing radium bromide (·33 mg. radium), backed by ebonite and covered with thin mica, was placed at 1 m. from the centre of the electroscope. The  $\beta$  and  $\gamma$  rays together caused a leaf-movement of 12·2 divisions/minute, and the  $\gamma$  rays alone of 0·4 division/minute. Since  $e^{\mu''} = 1·4$ , it follows that  $K/K' = 11·8 \times 1·4/·4 = 41$ . This is, however, too large, on account of the  $\beta$  rays from radium B reaching the electroscope. Kovarik\* has found, with aluminium screens,  $\mu = 13$  for radium C, and  $\mu = 75$  for radium B. Since  $\mu = ·0033$  for air in the case of the  $\beta$  rays from radium C,  $\mu = ·019$  for the  $\beta$  rays of radium B. If there are equal numbers of  $\beta$  particles from these two products, it can be readily shown that the  $\beta$  rays from radium C alone gave 10·9 D/m, corrected for air-absorption, so that  $K/K' = 27$ . This method involves some uncertainty.

2. A glass tube containing ·52 mg. of radium was placed at 75 cm. distance from the centre of the electroscope. The  $\beta$  rays gave 16·9, and the  $\gamma$  rays ·85 division/minute. The correction factor for air-absorption is 1·25, and for the glass walls about 1·40. The  $\beta$  rays from radium B were mainly absorbed. Thus

$$K/K' = \frac{16·9}{·85} \times 1·28 \times 1·40 = 35.$$

There is much uncertainty, however, in the correction for absorption by the glass walls, and by the radium bromide of one-quarter of full strength.

3. The most satisfactory method was the employment of a thin aluminium leaf (·0012 cm.), which had received a coating of the active deposit when negatively charged in the air above a solution of 11 mg. of radium bromide in a flask. Alternative readings for  $\beta$  and  $\gamma$  rays, and for the  $\gamma$  rays alone, were obtained, and the well-known decay-curve for the active deposit was plotted from the results, so that the ionization due to the  $\beta$  rays and to the  $\gamma$  rays respectively, at the same instant, could be found by interpolation. The

\* Phil. Mag. Nov. 1910.

leaf with the active deposit was hung by a thread at 50 cm. from the centre of the electroscope. When measuring the  $\gamma$  ray ionization, the  $\beta$  rays were partly absorbed by a zinc cylinder round the leaf, partly deflected by a powerful magnetic field. The electromagnet and cylinder were removed when the  $\beta$ -ray ionization was measured.

At a time when the radium B present was 57 per cent. of the radium C, the  $\beta$  rays gave 11.7 divisions/minute, and the  $\gamma$  rays 0.3. Hence, taking  $\mu = .0033$ , and  $\mu = .019$  for the two cases

$$x/1.17 + .57x/2.56 = 11.7.$$

$\therefore x = 10.9$ , the number of divisions a minute due to radium C alone, whence

$$K/K' = 10.9/0.3 = 36.$$

Again, when radium B was 29 per cent. of radium C in quantity, the  $\beta$  rays caused 7.5, and the  $\gamma$  rays .24 division/minute, so that

$$x/1.17 + .29x/2.56 = 7.5 \quad \text{and} \quad x = 7.8.$$

Hence

$$K/K' = 7.8/.24 = 33.$$

The mean value obtained in this way was  $K/K' = 34$ , and since  $K' = 3.74 \times 10^9$  from (1), it follows that

$$K = 1.27 \times 10^{11}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence the total number of ions produced by the  $\beta$  rays from one curie of radium C in air at atmospheric pressure is

$$4\pi K/\mu = 4\pi \times 1.27 \times 10^{11}/.004 = 4.0 \times 10^{14}. \quad . \quad (4)$$

The corresponding value for radium B is about 13/75 of this, or about

$$0.7 \times 10^{14}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

And, due to the  $\beta$  rays from both,  $4.7 \times 10^{14}$ .

(4) Instead of assuming the values for  $\mu$  as above, its value was actually determined for distances from 40 to 100 cm., and was found to be between .012 and .013. This magnitude suggests the joint effect of radium C and radium B. The value of  $\mu$  did not, however, appear to decrease with the time as the proportion of radium C to radium B increased. There seems to be, therefore, proceeding from radium C a large number of low velocity  $\beta$  rays, somewhat similar to those from radium B. If the value for  $K/K'$  is determined with a value for  $\mu$  intermediate between .004 and .012,

namely  $\cdot 008$ , I found from several experiments  $K/K' = 117$ , whence  $K = 4.35 \times 10^{11}$ , and

$$N = 4\pi \times 4.35 \times 10^{11} / \cdot 008 = 6.8 \times 10^{14}$$

including the rays from radium B.

It is quite clear that the total number of ions due to the  $\beta$  rays from a curie of radium C cannot be easily determined with any great precision, but the number lies between 4 and 6 times  $10^{14}$ .

The difficulties are:—

- (1) The presence of radium B.
- (2) The complex character of the  $\beta$  rays from radium C.
- (3) The uncertainty as to the entire removal of the  $\beta$  rays when measuring the  $\gamma$ -ray effect. The work requires repetition by those who are fortunate enough to be able to obtain a large amount of the active deposit of radium.

*Average total ions for one  $\beta$  particle, and ions per unit path.*

It has been found by Makower\* that a gramme of radium emits about  $5 \times 10^{10}$   $\beta$  particles per second, and theory suggests that radium B and radium C both emit  $3.4 \times 10^{10}$   $\beta$  particles per second, corresponding to the known number of  $\alpha$  particles.

If that is so,  $3.4 \times 10^{10}$   $\beta$  particles from one curie of radium C are producing about  $4 \times 10^{14}$  ions, and therefore one particle produces in an average path  $1.2 \times 10^4$  ions. As the average path is  $1/004$ , or 250 cm., it follows that a  $\beta$  particle produces about 48 ions per centimetre†. If the radius of a molecule is taken as  $10^{-8}$  cm., and the number of molecules in a cm.<sup>3</sup> of the atmosphere as  $N = 2.7 \times 10^{19}$ , it follows, from the formula of Clausius, that the mean path between collisions by a  $\beta$  particle with air molecules, at atmospheric pressure, is

$$L = 1/N\pi\sigma^2 = 1/8500 \text{ cm.},$$

so a  $\beta$  particle ionizes only about 48 ions out of every 8500 molecules which it directly encounters. Unless the  $\beta$  particle is an adept at swerving, it must pass right through 180 molecules for every one which it succeeds in ionizing. Or, on the other hand, if every collision were supposed successful

\* Phil. Mag. Jan. 1909.

† Cf. Durack, Phil. Mag. May 1903, who found a mean path of 6 cm. for a  $\beta$  particle in air at 2 mm. pressure.

in ionizing, the radii of the molecules would have to be as small as  $8 \times 10^{-10}$  cm.

If the supposition were made that a  $\gamma$  ray is an entity with a linear path, and if it were further assumed that  $3.4 \times 10^{10}$  such entities were ejected from a curie of radium C every second, it follows that one such entity, on an average path of 250 metres, makes  $10.6 \times 10^{14} / 3.4 \times 10^{10}$ , or 30,000 ions, or 1.2 ions per cm. of path. In this case only one collision in every 7000 is effective in producing an ion.

In Townsend's work on 'Ionization of Gases by Collision,' it appears to be proved that at low pressures practically every encounter of a negative ion is effective in ionizing, provided the velocity exceeds a certain limit. It seems certain, therefore, that the  $\beta$  particle pierces the molecule in its flight, and that ionization results only in about 2 per cent. of the collisions.

### *Heating Effect.*

It has been shown by Rutherford and Geiger \* that the  $\alpha$  particles from a gramme of radium and from its three succeeding  $\alpha$ -ray products, produce  $244 \times 10^{14}$  ions per second. The heating effect is about 110 calories per hour, the greater part of which is due to the  $\alpha$  particles. It appears from recent work by Geiger † that the  $\alpha$  particles expend nearly the whole of their energy in ionization. It is thus possible to calculate from my determinations the heating effects due to the  $\beta$  and  $\gamma$  rays from a curie of radium C, making the assumption that the energy expended in ionization is a measure of their heating effects when absorbed.

Rays.	Total ions per second.	Calories/hour.
$\alpha$ .....	$244 \times 10^{14}$	103.5
$\beta$ .....	$5 \times 10^{14}$	2.0
$\gamma$ .....	$10.2 \times 10^{14}$	4.5
		<u>110</u>

Thus, the  $\beta$  and  $\gamma$  rays together contribute 6 per cent. of the total heat, and the  $\gamma$  rays alone 4 per cent.‡ This result

\* Proc. Roy. Soc. A. lxxxi. p. 141.

† Proc. Roy. Soc. A. lxxxiii. p. 505.

‡ Rutherford, 'Radioactivity,' p. 200, has calculated the energy ratio for  $\alpha$  and  $\beta$  particles as 83 for a  $\beta$  particle with velocity  $1.5 \times 10^9$ .

agrees well with the measurements of Rutherford and Barnes, who obtained an increase of about two calories an hour, when about one-half to one-third of the  $\gamma$  rays were absorbed in a lead cylinder.

The energy required to make an ion may be calculated from any of the above relations, and the results must, of course, be concordant.

The value obtained is  $5.2 \times 10^{-11}$  erg per ion. If the work required to produce an ion is  $e^2/r$ , where  $r$  is the radius of a molecule, it follows that the radius of a molecule is  $0.46 \times 10^{-8}$  cm., a result of the right order, but apparently somewhat small. Townsend has found that the minimum energy required to make an ion is  $2.5 \times 10^{-11}$  erg.

If the old view of the  $\gamma$  rays is examined, which supposed that the expulsion of a  $\beta$  particle caused an electromagnetic pulse with uniform distribution of energy near a spherical shell, some remarkable results follow. The work of Wulf \* on the penetration radiation on the Eiffel Tower indicates that the  $\gamma$  rays from radium and thorium in the earth reach a height of 300 metres, and ionize there. This paper shows that the mean range of a  $\gamma$ -ray disturbance is 250 metres. It has already been pointed out that Townsend found the minimum energy required to make an ion to be  $2.5 \times 10^{-11}$  erg, and that such an ion may be produced by  $\gamma$  rays at 300 m. from the radioactive source. If  $A$  is the area of the cross-section of a molecule, we have over a surface  $A$  at distance 250 m. from the centre at least  $2.5 \times 10^{-11}$  erg. Therefore, over surface  $A$  at 1 cm. from the source there must be an energy  $2.5 \times 10^{-11} \times (25,000)^2$ , or  $\cdot 0156$  erg.

As about  $3.4 \times 10^{10}$   $\beta$  particles leave a curie of radium C every second, there will be the same number of  $\gamma$  pulses, and we have  $3.4 \times 10^{10} \times \cdot 0156$ , or  $5 \times 10^8$  ergs per second, as a very moderate estimate of the power of the  $\gamma$  radiation.

But the whole power of all the radiations from a gramme of radium is only  $1.3 \times 10^6$  ergs per second!

It therefore seems impossible to consider the radiation as a spherical shell with uniform energy over the surface, and also impossible to contemplate the  $\gamma$  radiation as expanding conically. It must be linear, whether electromagnetic or corpuscular. As the  $\gamma$  radiation is mainly independent of the concentration at the source, it does not seem possible to conjure up a train of pulses, or overlapping of pulses, or any such interference effects to account for the energy necessary for ionization.

\* *Phys. Zeit.* Sept. 15, 1910.

It seems, then, correct to speak of a  $\gamma$  ray in the sense of a definite entity carrying energy in a linear path, unless, indeed, most of the energy of ionization comes from the molecule ionized, a view which is generally rejected.

*Summary.*

1. The value of the constant  $K'$  for  $\gamma$  rays, which may be given the theoretical definition of the number of ions produced per cm.<sup>3</sup> per second at a distance of 1 cm. from a curie of radium C, in air at atmospheric pressure, is  $3.74 \times 10^9$ . The total number of ions per second which the  $\gamma$  rays from a curie of radium C could produce in air at atmospheric pressure is  $N' = 1.1 \times 10^{15}$ .

2. Corresponding values for the  $\beta$  rays have been found approximately, namely,  $K = 1.3 \times 10^{11}$ , and  $N = 4.0 \times 10^{14}$ .

3. Hence, the total number of ions made by one  $\beta$  particle in an average flight from radium C in the atmosphere is  $1.2 \times 10^4$ , equivalent to about 48 ions per cm. Hence, the  $\beta$  particle must pass through about 180 molecules for every one which it ionizes, if the radius of a molecule is  $10^{-8}$  cm. The values in (2) and (3) are only approximations.

4. If the  $\gamma$  ray is an entity with a linear path, the total ions per entity are  $3 \times 10^4$  for an average flight, and 1.2 ions per cm. of path.

5. The heating effect of the  $\beta$  and  $\gamma$  rays may be calculated on the assumption that ionization is a measure of the energy expended. If a gramme of radium, and its four succeeding products, have a heating effect of 110 calories per hour, then the distribution is somewhat as follows:—

$\alpha$ rays.....	103.5	calories.
$\beta$ „ .....	2.0	„
$\gamma$ „ .....	4.5	„

6. The energy expended in making an ion is calculated as  $5.2 \times 10^{-11}$  erg, and the radius of the molecule as  $4.6 \times 10^{-8}$ , a result which is of the right order, but probably too small.

Montreal,  
April, 1911.

LIH. *Note on the Production of Nuclei in Air by Intense Cooling.* By GWILYM OWEN, M.A., D.Sc., University of Liverpool\*.

IF a sealed glass bulb containing moist dust-free air be plunged into liquid air, a dense cloud may be seen forming inside the bulb. On removing the liquid air and allowing the bulb and contents to warm up to atmospheric temperature, the drops evaporate and the cloud disappears. This effect is, of course, the cloud-like condensation which C. T. R. Wilson† has shown to take place when a moist dust-free gas is subjected to a sudden expansion of magnitude 1·38, the nuclei of condensation being accidental aggregations of water-molecules which appear to be always present in saturated water-vapour. If a similar experiment be tried with a *dry* gas (such as is obtained from boiling liquid air), then no *visible* cloud can be observed on cooling the bulb in the way described. It has, however, been shown‡ that even in the dry gas large numbers of small particles are produced by the cooling process. These particles are not visible directly, but their presence can be shown by admitting some of the gas into a Wilson expansion apparatus§ and subjecting it to a sudden expansion (of magnitude 1·15 about). The water-vapour in the expansion apparatus thus condenses round the invisible particles, and a dense cloud is obtained. It may also be remarked that so low a temperature as that of liquid air is not necessary for the production of these nuclei. A temperature of  $-120^{\circ}$  C. is sufficient.

Now it is obvious that no definite conclusion can be drawn regarding the origin and nature of these nuclei produced in a gas by intense cooling if there is any doubt as to the gas being really dry. For, if the gas contains only traces of moisture we may explain the effect as being due to the formation (at the very low temperature) of aggregations of water-molecules, too small to be themselves visible, but yet sufficiently large to be in equilibrium and to act as condensation nuclei.

On the other hand, if we suppose that the precautions taken by Owen and Hughes to obtain dry air warrant the assumption that the cooled gas was as free from water-vapour as it can possibly be obtained, then it is necessary to consider the view tentatively suggested by them, namely, that the

\* Communicated by the Author.

† C. T. R. Wilson, Phil. Trans. clxxxix. p. 265 (1897).

‡ G. Owen & A. Ll. Hughes, Phil. Mag. Oct. 1907, June 1908.

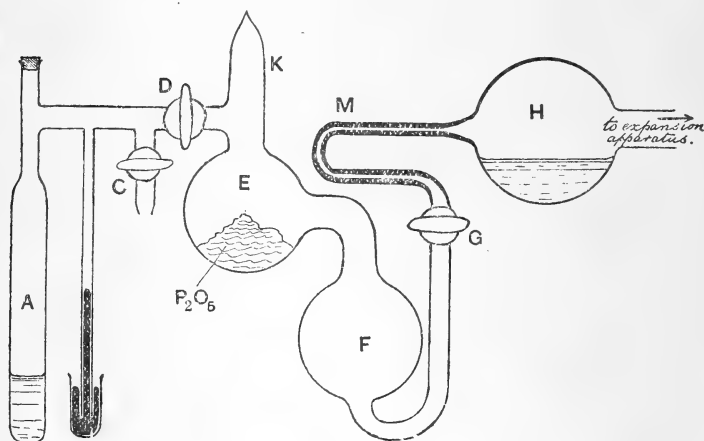
§ C. T. R. Wilson, Proc. Camb. Phil. Soc. p. 333 (1897).

nuclei are aggregations, not of water-molecules but of air-molecules, brought into existence by the approach of the gas to its condensing point; in other words, that the nuclei afford evidence of the occurrence of *incipient liquefaction* in a gas at a temperature well above its real liquefying point.

An experiment to decide *definitely* between these two views would appear to be impossible, for a *perfectly dry* gas has probably never been obtained. The present note, however, contains a brief account of a further attempt to eliminate traces of water-vapour from the gas experimented upon. The result obtained supports the view that the nuclei are aggregations of air-molecules.

Owen and Hughes (*loc. cit.*) obtained their dry air from boiling liquid air. The same method was adopted in the present experiment, with this difference—that the air so obtained was sealed up in contact with  $P_2O_5$  for several weeks before it was subjected to the cooling process. The amount of water-vapour ultimately left in a closed space containing  $P_2O_5$  is generally regarded as being extremely small. This method of drying a gas is, for example, sufficiently effective to stop entirely several chemical actions requiring the merest trace of moisture, such as the combination of hydrogen and chlorine under the influence of light.

The arrangement used in the present experiment is shown in the figure. The air to be cooled was contained in the



glass bulb F some 5 cms. in diameter, connected by a wide tube to a second bulb E, which served to hold the  $P_2O_5$ . The globe H is the cloud-chamber, connected to a Wilson expansion apparatus, and in which the air is tested for the



presence of nuclei after the cooling process. H was connected to FG through the long capillary tube M, the object of which was to prevent diffusion of moisture from H into F during the operation of filling the latter with dry air. Before the  $P_2O_5$  was placed in the bulb E the whole apparatus to the left of G was thoroughly dried by allowing a current of dry air (obtained from the liquid air stored in A) to stream through for a considerable time, the tubes and bulbs meanwhile being strongly heated with a flame. Finally  $P_2O_5$  was introduced through K which was sealed off, and the taps D and G closed. The efficiency of this method of drying the apparatus was shown by the fact that the  $P_2O_5$  preserved indefinitely its dry and powdery condition. Hence no appreciable amount of moisture could have remained in the apparatus, even before the  $P_2O_5$  was introduced.

After the air in E, F had been in contact with the  $P_2O_5$  for three weeks, the bulb F was surrounded by liquid air for about one minute and then allowed to regain atmospheric temperature. Its contents were then quickly driven into the cloud-chamber in the following way. Some liquid air had previously been placed in A and allowed to boil away through C until the space between A and D was wholly free from dusty air. The cloud-chamber and expansion apparatus had also been previously exhausted to a pressure of about half an atmosphere. Thus when F had regained atmospheric temperature, the taps D and G were opened and the air in the bulbs driven by a stream of dust-free air into the cloud-chamber. G was then closed and the pressure in H adjusted so as to admit of an expansion of about 1.15, corresponding to a pressure fall of some 10 cm. of mercury. *The result of this expansion was a coloured cloud*, showing that the severe cooling process through which the well-dried air had passed had resulted in the formation of a very large number of nuclei.

Control experiments were carried out in exactly the same way, omitting only the cooling of the bulb F. Under these conditions no drops were seen in the cloud-chamber on expanding.

One other point required testing beforehand. Simple calculation showed that the pressure of the air in EF would fall to about half an atmosphere when F was surrounded by the liquid air. Now this fall of pressure might conceivably liberate dusty air or other particles from the  $P_2O_5$ . It was shown, however, in the following way that this complication did not occur. The dried air in EF was expanded from atmospheric pressure to half an atmosphere by connecting

the bulb with an exhausted chamber. Dust-free air from A was then admitted, and the air remaining in EF driven along into the cloud-chamber in the way already described. No cloud, not even a shower, was obtained on expanding, showing that the fall of pressure in the bulbs had not liberated nuclei from the  $P_2O_5$ . Thus the nuclei on which the coloured cloud was subsequently obtained must have been the result of the cooling process through which the air had passed.

### *Conclusion.*

The experiment shows that if dust-free air, dried by standing for three weeks over phosphorus pentoxide, be cooled to a very low temperature, such as that of liquid air, large numbers of small invisible nuclei are produced in the gas. It is difficult, however, to decide with absolute certainty whether these particles are aggregations of *water*-molecules or of *air*-molecules. Owen and Hughes, in their original papers, were led to suggest the latter, that is, the *air*-molecule, hypothesis. The result of the experiment described in the present note supports that view.

Holt Physics Laboratory,  
University of Liverpool,  
April 7, 1911.

LIV. *Molecular Attraction and the Properties of Liquids.*  
By R. D. KLEEMAN, D.Sc., B.A., Mackinnon Student of  
the Royal Society, and Clerk Maxwell Student of the  
University of Cambridge\*.

IN a previous paper the writer has shown that an infinite number of equations can be obtained connecting the internal heat of evaporation or surface tension of a liquid with its temperature, density, and density of the saturated vapour †. These equations can be deduced by means of the law of attraction between molecules obtained from the surface tension of liquids on giving the arbitrary function in the law various appropriate forms. On equating the various expressions obtained for the surface tension or latent heat, useful equations connecting the other quantities relating to a liquid may be obtained ‡. Examples of the foregoing results are given in the papers quoted. The subject will be further developed in this paper.

\* Communicated by the Author.

† Phil. Mag. Jan. 1911, pp. 83-102.

‡ Phil. Mag. March 1911, p. 352.

As we shall frequently have to refer to the general equations for the internal heat of evaporation and surface tension deduced in a previous paper, they will be placed in this paper in a form convenient for our purpose. The heat of evaporation  $L$  is given by the equation

$$L = \frac{(\sum \sqrt{m_1})^2}{m} x_a \left[ \int, \Sigma \right]_{n, w, u, v} \cdot \phi_2 \left( \frac{z_1}{x_c}, \frac{T}{T_c} \right) \cdot \frac{x_a(n+w)}{z_1^6} \\ - \frac{(\sum \sqrt{m_1})^2}{m} x_b \left[ \int, \Sigma \right]_{n, w, u, v} \cdot \phi \left( \frac{z_2}{x_c}, \frac{T}{T_c} \right) \cdot \frac{x_b(n+w)}{z_2^6} \cdot \cdot \cdot \quad (1)$$

where

$$z_1 = x_a \sqrt{\{n+w\}^2 + u^2 + v^2},$$

and

$$z_2 = x_b \sqrt{\{n+w\}^2 + u^2 + v^2},$$

$m$  denotes the molecular weight of the liquid, and  $\sum \sqrt{m_1}$  the sum of the square roots of the atomic weights of a molecule,  $T$  is the temperature of the liquid and  $T_c$  the critical temperature,  $x_a$  and  $x_b$  are the distances of separation of the molecules of the liquid and saturated vapour respectively, and  $x_c$  the distance at the critical temperature. If the critical density and the density of the liquid and saturated vapour be denoted by  $\rho_c$ ,  $\rho_1$ , and  $\rho_2$  respectively, we have

$$x_c = \left( \frac{m}{\rho_c} \right)^{1/3}, \quad x_a = \left( \frac{m}{\rho_1} \right)^{1/3}, \quad \text{and} \quad x_b = \left( \frac{m}{\rho_2} \right)^{1/3}.$$

The symbol  $\left[ \int, \Sigma \right]_{n, w, u, v}$  in the equation is an integral and summation operator between given limits applying to the quantities  $n, w, u$ , and  $v$ , on its right-hand side: we are not concerned with its exact form in this paper. This equation follows from an investigation by the writer\*, taking the attraction between two molecules to be given by

$$\phi_2 \left( \frac{z}{x_c}, \frac{T}{T_c} \right) \cdot \frac{(\sum \sqrt{m_1})^2}{z^5},$$

where  $z$  is their distance of separation. This law of attraction was deduced from surface tension and heat of evaporation data, which leaves the form of the function

$$\phi_2 \left( \frac{z}{x_c}, \frac{T}{T_c} \right) \text{ arbitrary } \dagger.$$

\* Phil. Mag. May 1910, pp. 793-795.

† Loc. cit. pp. 791-793.

Similarly we have for the surface tension  $\lambda$  the equation

$$\lambda = \frac{(\Sigma \sqrt{m_1})^2}{x_{ab}} \left\{ \int, \Sigma \right\}_{n, w, u, v} \cdot \phi_2 \left( \frac{z_{12}}{x_c}, \frac{T}{T_c} \right) \cdot \frac{x_{ab}(n+w)}{z_{12}^6}, \quad (2)$$

where

$$z_{12} = x_{ab} \sqrt{\{(n+w)^2 + u^2 + v^2\}},$$

$$\text{and } x_{ab} = \left( \frac{m}{\rho_1 - \rho_2} \right)^{1/3}, \quad \text{and } \left\{ \int, \Sigma \right\}_{n, w, u, v}, \quad \text{as before,}$$

denotes an operator between given limits. This equation follows from an investigation given in the same paper as that on the heat of evaporation.

The various forms of the arbitrary function that satisfy the above equations must be found by trial: we have already referred to some examples at the beginning of the paper. But it will be easily seen that we can give the function almost any form we please provided its real values are not restricted to lie between certain limits, and it contains a sufficiently large number of terms or independent constants. Further, the equations enable us to determine the nature of the constants in any empirical relation of the heat of evaporation or surface tension with other quantities, by giving the arbitrary function a form that gives the relation required and comparing the constants obtained with those contained in the empirical relation. Examples of this will be given in this paper.

### *Surface Tension.*

If we put

$$\phi_2 \left( \frac{z_{12}}{x_c}, \frac{T}{T_c} \right) = \frac{z_{12}^6}{x_c^6} a \left( 1 + \frac{\alpha T}{T_c} = \frac{\beta T^2}{T_c^2} + \dots \right)$$

in the formula for the surface tension, we obtain

$$\lambda = \left( \frac{\rho_c \Sigma \sqrt{m_1}}{m} \right)^2 a_1 \left( 1 + \frac{\alpha_1 T}{T_c} + \frac{\beta T^2}{T_c^2} + \dots \right),$$

where  $a_1, \alpha_1, \beta_1 \dots$ , are constants which are the same for all liquids. An equation of the form  $\lambda = A(1 + TB)$  has already been used by physicists to represent the surface tension, and found to agree approximately with the facts. The former of the above equations indicates the nature of the constants involved.

Before proceeding it will be of importance to consider a point in connexion with testing the truth of relations deduced theoretically. It may happen—and in most cases does

happen—that the empirical relation is of such a form that the relative value of the constants may be varied over a considerable range without affecting the agreement of the relation with the facts. In that case, slight errors in the data used may give rise to constants which are far from being equal to those deduced theoretically. The proper way, therefore, to test whether the theoretical constants fit in with the facts is to assume that they do and then determine whether the constants which are to be the same for each substance (numerical factors) approximately fulfil that condition. It cannot be too strongly emphasized in this kind of work that starting out with some law and deducing relations from it, their good or bad agreement with the facts may in part be due to the mathematical form of the relations in connexion with the experimental errors of the quantities involved.

Van der Waals has proposed the equation  $\lambda = C \left(1 - \frac{T}{T_c}\right)^D$

for the surface tension and applied it to the facts\*. It was found that D is very nearly the same for the substances examined, viz., ethyl oxide, benzene, methyl formate, chlorobenzene, carbon-tetrachloride, being equal to about 1.23; while the values found for C were 57.68, 69.02, 64.57, 67.14, and 64.71, respectively. Assuming D constant the equation is obtained by putting

$$\phi_2 = \frac{z_{12}^6}{a_c^6} a \left(1 - \frac{T}{T_c}\right)^D$$

in the general equation for the surface tension; which gives

$$C = b \left( \frac{\rho_c \Sigma \sqrt{m_1}}{m} \right)^2,$$

where  $b$  is a constant. The values of C for the above substances are thus proportional to  $9.6 \times 10^{-3}$ ,  $12 \times 10^{-3}$ ,  $9.8 \times 10^{-3}$ ,  $10.9 \times 10^{-3}$ , and  $10.6 \times 10^{-3}$ , respectively. These values are approximately proportional to those given by Van der Waals.

If we put

$$\phi_2 = \frac{z_{12}^4}{a_c^4} a \left(1 - \frac{\alpha T}{T_c} - \dots\right)$$

the equation for the surface tension becomes

$$\lambda = b \left( \frac{\rho_c}{m} \right)^{4/3} (\Sigma \sqrt{m_1})^2 \left( \frac{\rho_1 - \rho_2}{m} \right)^{2/3} \left(1 - \frac{\alpha T}{T_c} - \dots\right).$$

\* *Zeitsch. f. phys. Chemie*, xiii. p. 716 (1894).

By means of equation (5) it may be transformed into

$$\lambda = k \left( \frac{\rho_1 - \rho_2}{m} \right)^{2/3} (T_c - \alpha T - \dots), \dots \dots \dots (1)$$

where  $k$ ,  $\alpha$ , &c., are universal constants. If we neglect the powers of  $T$  higher than the first and put  $\alpha = 1$ , the equation for low temperatures becomes

$$\lambda = k \left( \frac{\rho_1}{m} \right)^{2/3} (T_c - T),$$

which is Eötvös' famous equation. It is known that it does not agree well with the facts near the critical point. The preceding equation shows what modifications must be introduced to obtain a better agreement. Equation (1) is the fundamental form of Eötvös' equation based on the law of attraction between molecules. The writer found that a good agreement is usually obtained by retaining only the first power of  $T$ , and giving  $\alpha$  an appropriate value. This is shown by Table I. which contains the value of  $k$  for

TABLE I.

ETHYL OXIDE. $\alpha = 1.006.$				METHYL FORMATE. $\alpha = 1.003.$			
T.	$k$ .	T.	$k$ .	T.	$k$ .	T.	$k$ .
293	2.11	383	2.06	293	1.99	383	1.98
313	2.11	393	2.06	303	1.99	393	1.99
323	2.09	403	2.05	313	1.99	403	1.98
333	2.07	403	2.05	323	1.99	413	2.02
343	2.07	423	2.02	333	1.99	423	1.97
353	2.07	433	2.03	343	1.99	433	1.96
363	2.07	443	2.05	353	1.99	443	1.95
373	2.07	453	2.07	363	1.99	453	1.95
				373	1.99	463	1.92

two liquids calculated by the above formula, giving  $\alpha$  the values placed at the top of the table. The data used for the calculations were taken from a paper by Ramsay and Shields\*. It will be seen that  $k$  is practically independent of the temperature and nature of the liquid. The values of  $\alpha$  for the substances ethyl acetate, carbon tetrachloride,

\* Phil. Trans. R. Soc. A. vol. clxxxiv, p. 647 (1893).

benzene, and chlorobenzene were found to be equal to 1.003, 1.004, 1.002, and 1.104, respectively; they are practically equal to one another, as they should be, and differ little from unity. The fundamental form of Eötvös' equation, it will be seen, gives  $\lambda=0$  at the critical point.

It may be mentioned that a fair agreement with the facts is also obtained by using the empirical equation

$$\lambda = \frac{k}{m^{2/3}} (\rho_1^{2/3} - \rho_2^{2/3}) (T_c - T).$$

Another equation for the surface tension of interest may be pointed out here. If  $\phi_2$  is put equal to

$$\frac{z_{12}^7 a}{x_c^7} \left( 1 + \frac{\alpha T}{T_c} + \dots \right)$$

in the surface tension equation we obtain

$$\lambda = c \left( \frac{\rho_c}{m} \right)^{7/3} (\Sigma \sqrt{m_1})^2 \left( \frac{m}{\rho_1 - \rho_2} \right)^{1/3} \left( 1 + \frac{\alpha T}{T_c} + \dots \right).$$

By means of equation (6) it may be transformed into

$$\lambda = K p_c \left( \frac{m}{\rho_1 - \rho_2} \right)^{1/3} \left( 1 + \frac{\alpha T}{T_c} + \dots \right),$$

where  $K$  is a universal constant. At corresponding states we should therefore have that  $\frac{\lambda}{p} \left( \frac{\rho_1 - \rho_2}{m} \right)^{1/3}$  has the same value for all liquids. That this is approximately the case is shown by Table II.

TABLE II.

	$\frac{2T_c}{3}$	$\lambda$	$\rho_1 - \rho_2$	$m$	$p_c$	$\frac{\lambda}{p_c} \left( \frac{\rho_1 - \rho_2}{m} \right)^{1/3}$
Ether.....	311.7	14.19	.6857	74	36.28	$8.4 \times 10^{-2}$
Methyl formate .....	324.7	19.80	.9250	60	56.62	8.7 „
Carbon tetrachloride.	371.0	16.69	1.4285	154	44.97	7.8 „
Benzene.....	374.3	17.87	.7881	78	47.89	8.1 „
Chlorobenzene .....	422.0	17.78	.9544	112.5	44.62	8.1 „

Whittaker\* has shown that  $\lambda - T \frac{d\lambda}{dT} = E = KLT$ , where  $E$  is the potential energy per  $\text{cm}^2$  of liquid surface, and  $K$  is a constant which depends only on the nature of the liquid. The writer has shown that  $K = M \frac{m^{1/3} \rho_c^{3/2}}{T_c}$ , where  $M = 5.57 \times 10^{-1}$ . We will now find the form of the arbitrary function in the law of molecular attraction to which this relation corresponds. From equation (4) we have

$$L = \left( A_1 - A_2 \frac{n_2^{4/3}}{n_1^{4/3}} \right) \frac{\rho_1^{4/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2,$$

where  $A_1$  and  $A_2$  are each the same for corresponding states being functions of  $\phi_2$ , which in  $A_1$  is a function of  $n_1$  and  $n_3$ , and in  $A_2$  a function of  $n_2$  and  $n_3$ , where  $\rho_1 = n_1 \rho_c$ ,  $\rho_2 = n_2 \rho_c$ , and  $T = n_3 T_c$ . We have therefore

$$E = LTM \frac{m^{1/3} \rho_c^{2/3}}{T_c} = \left( A_1 - A_2 \frac{n_2^{4/3}}{n_1^{4/3}} \right) \frac{M n_3}{n_1^{2/3}} \left( \frac{\rho_1}{m} \right)^2 (\Sigma \sqrt{m_1})^2.$$

By means of equation (3) we obtain

$$E = \lambda - T \frac{d\lambda}{dT} = \left\{ \kappa''' \left( 1 - \frac{n_2}{n_1} \right)^2 - n_3 \left( 1 + \frac{n_2}{n_1} \right)^2 \frac{d\kappa'''}{dn_3} - \kappa''' \left( 1 - \frac{n_2}{n_1} \right) 2n_3 \left( \frac{1}{n_1} \frac{dn_1}{dn_3} - \frac{1}{n_2} \frac{dn_2}{dn_3} \right) \right\} \left( \frac{\rho_1}{m} \right)^2 (\Sigma \sqrt{m_1})^2,$$

where  $\kappa'''$  is a function of  $\phi_2$ , and this a function of  $n_3$  and  $(n_1 - n_2)$ . If the above two expressions for  $E$  be equated we get an equation containing  $n_1$ ,  $n_2$ , and  $n_3$  only, as should be the case since  $\phi_2$  is a function of these quantities. The form of  $\phi_2$  to which the above relation corresponds is therefore that which reduces this equation to an identity.

#### *Internal Heat of Evaporation.*

Suppose we substitute

$$\frac{z_{12}^4}{x_c^4} \alpha_1 \left( 1 + \frac{\alpha T}{T_c} + \frac{\beta T^2}{T_c^2} + \dots \right)$$

for  $\phi_2$  in the general equation for the internal heat of evaporation. We then obtain

$$L = \frac{(\Sigma \sqrt{m_1})^2}{m^{7/3}} \rho_c^{4/3} b_1 \left( 1 + \frac{\alpha T}{T_c} + \frac{\beta T^2}{T_c^2} + \dots \right),$$

\* Proc. Roy. Soc. A, vol. lxxxi, p. 21 (1908); Phil. Mag., July 19 09 p. 39.



an equation that is sometimes useful. Since the heat of evaporation is zero at the critical point we must have

$$1 + \alpha + \beta + \gamma + \dots = 0.$$

An interesting case is obtained when  $\phi_2$  is put equal to  $\frac{\sim 12}{x_c^7} \cdot \phi_x \left( \frac{T}{T_c} \right)$  in the general equation for the heat of evaporation, where  $\phi_x \left( \frac{T}{T_c} \right)$  is a function of  $\frac{T}{T_c}$ . The equation then becomes

$$L = \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right) c_1 (\Sigma \sqrt{m_1})^2 \left( \frac{\rho_c}{m} \right)^{7/3} \cdot \phi_x \left( \frac{T}{T_c} \right),$$

where  $c_1$  is a numerical constant. Substituting this value of  $L$  in Clapeyron's equation

$$L = \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right) \left( T \frac{dp}{dT} - p \right),$$

where  $p$  denotes the pressure of the saturated vapour, we obtain

$$c_1 (\Sigma \sqrt{m_1})^2 \left( \frac{\rho_c}{m} \right)^{7/3} \cdot \phi_x \left( \frac{T}{T_c} \right) = T \frac{dp}{dT} - p. \quad (2)$$

Dividing by  $T_2$  and integrating we obtain

$$\frac{p}{T} = C + c_1 (\Sigma \sqrt{m_1})^2 \left( \frac{\rho_c}{m} \right)^{7/3} \int \phi_x \left( \frac{T}{T_c} \right) \cdot \frac{dT}{T^2},$$

where  $C$  is an arbitrary constant whose value can be obtained in terms of the critical quantities by applying the equation to the critical point. By choosing the form of

$\phi_x \left( \frac{T}{T_c} \right)$  so that the above integral can be evaluated we can pass at once from a formula for the internal heat of evaporation to one connecting  $p$  and  $T$ , and in which all the constants are determined.

If we are given an empirical relation connecting  $p$  and  $T$  we can determine the nature of the constants it contains by means of equation (2). This is best illustrated by an example. Let us take the equation

$$\log p = A - \frac{B}{T} - C \log T,$$

which perhaps better than any other agrees with the facts\*.

\* Winkelmann's *Handbuch der Physik*, Wärme, sec. edition, p. 957.

Substituting for  $p$  from this equation in equation (2) we obtain

$$c(\Sigma\sqrt{m_1})^2\left(\frac{\rho_c}{m}\right)^{7/3} \cdot \phi_x\left(\frac{T}{T_c}\right) = \frac{e^A e^{-B/T}}{T^C} \left(\frac{B}{T} - C - 1\right).$$

It will be seen that the right-hand side of this equation must be a function of the ratio  $\frac{T}{T_c}$ , and we therefore have that  $B = \alpha T_c$ , where  $\alpha$  and  $C$  are universal constants. Further,  $e^A$  contains the factor  $T_c^C$ , and therefore

$$e^A/T_c^C = c(\Sigma\sqrt{m_1})^2\left(\frac{\rho_c}{m}\right)^{7/3}.$$

The vapour pressure equation then becomes

$$\log p = \log \left( T_c^C c(\Sigma\sqrt{m_1})^2 \left(\frac{\rho_c}{m}\right)^{7/3} \right) - \frac{\alpha T_c}{T} - C \log T.$$

The corresponding equation for the internal heat of evaporation is

$$L = \left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right) c(\Sigma\sqrt{m_1})^2 \left(\frac{\rho_c}{m}\right)^{7/3} \left(\frac{T_c}{T}\right)^C e^{-\frac{\alpha T_c}{T}} \left(\frac{\alpha T_c}{T} - C - 1\right).$$

By equating two different formulæ for the internal heat of evaporation we obtain a relation between the quantities  $T$ ,  $T_c$ ,  $\rho_1$ ,  $\rho_2$ , and  $\rho_c$ . We have already given examples of this in a previous paper. Since the equation for the heat of evaporation may within certain restrictions be given any form we please, this applies also to the equations obtained in the above way. An example which is of interest will be given in this paper. Let us put

$$\phi_2 = \frac{z_{12}}{x_c} \left(1 + \frac{\alpha T}{T_c} + \frac{\beta T^2}{T_c^2} + \dots\right)$$

in the general equation for the heat of evaporation, and we obtain

$$L = (\rho_1 - \rho_2) c_2 \left(1 + \frac{\alpha T}{T_c} + \frac{\beta T^2}{T_c^2} + \dots\right) \frac{(\Sigma\sqrt{m_1})^2 \rho_c^{1/3}}{m^{7/3}},$$

where  $c_2$  is a numerical constant. An equation for the heat of evaporation which we have already established\* is

$$L = c_3 (\rho_1^2 - \rho_2^2) \frac{(\Sigma\sqrt{m_1})^2}{m^{7/3} \rho^{2/3}},$$

where  $c_3$  is a numerical constant. Equating these two

\* Phil. Mag. Oct. 1910, p. 678.

values of  $L$  we obtain

$$\rho_1 + \rho_2 = k \rho_c \left( 1 + \frac{\alpha T}{T_c} + \frac{\beta T^2}{T_c^2} + \dots \right),$$

where  $k$  is a numerical constant. If the terms containing higher powers of  $T$  than the first be omitted, the equation expresses what is known as Cailletet and Mathias' linear diameter law. This law agrees well with the facts. The nature of the constants in the equation, it may be pointed out, are the same as would be obtained by applying the equation to the critical and the absolute zero of temperature.

We have thus another simple equation for the internal heat of evaporation, viz.,

$$L = c_2(\rho_1 - \rho_2) \left( 1 + \frac{\alpha T}{T_c} \right) \frac{(\Sigma \sqrt{m_1})^2}{m^{7/3}} \rho_c^{1/3}.$$

According to this equation  $\frac{L}{\rho_1 - \rho_2}$  is proportional to

$$\frac{(\Sigma \sqrt{m_1})^2}{m^{7/3}} \rho_c^{1/3},$$

for all liquids at corresponding states. That this is the case is shown by Table III., which contains the values of  $\frac{L}{\rho_1 - \rho_2}$  for

TABLE III.

	$L$ .	$\Sigma \sqrt{m_1}$	$\rho_c$ .	$\frac{L}{\rho_1 - \rho_2}$ .	$\frac{\rho_c^{1/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2 5711$ .
Ether .....	75.44	27.84	.2604	110.0	122.8
Carbon tetrachloride.	39.87	27.30	.5576	27.9	27.6
Benzene .....	81.73	26.76	.3045	103.7	105.9
Methyl formate .....	92.85	18.92	.3489	100.3	92.2
Chlorobenzene .....	65.88	31.72	.3654	69.0	67.3

temperatures of  $\frac{2T_c}{3}$  obtained from the values of  $L$  calculated by Mills\*, and the values of  $\frac{(\Sigma \sqrt{m_1})^2 \rho_c^{1/2}}{m^{7/3}}$  multiplied by 5711. The agreement between the two sets of values is fairly good.

\* Journ. of Phys. Chem. vol. viii. p. 405 (1904).

*The Values of some Corresponding Quantities.*

The various formulæ that we have deduced from the law of attraction between molecules given at the beginning of the paper, contain a number of constants each of which has the same value for all liquids at corresponding temperatures, being functions of the arbitrary function in the law of attraction. Expressions for these constants can be found when the formulæ apply to a liquid and its saturated vapour, that is, when the state of the substance is a function of the temperature only. We are enabled to do this owing to the fact that an infinite number of equations can be found connecting the internal heat of evaporation and surface tension with other quantities. We have already deduced some results along this line\*; we are now able to improve upon and extend them.

The fundamental equation for the surface tension determined directly from the law of attraction between molecules is

$$\lambda = \kappa''' \left( \frac{\rho_1 - \rho_2}{m} \right)^2 (\Sigma \sqrt{m_1})^2, \dots \dots \dots (3)$$

where  $\kappa'''$  is a constant which is the same for all liquids at corresponding temperatures†. In subsequent transformations we will use the relations  $\rho_1 = n_1 \rho_c$ ,  $\rho_2 = n_2 \rho_c$ ,  $T = n_3 T_c$ ,  $p = n_4 p_c$ , and  $\rho_0 = b \rho_c$ , the quantities  $n_1$ ,  $n_2$ ,  $n_3$ ,  $n_4$ , and  $b$  being of course the same for all liquids at corresponding states. At the absolute zero we then have

$$\lambda_0 = \kappa_0''' \frac{b^2 \rho_c^2}{m^2} (\Sigma \sqrt{m_1})^2 = \frac{\kappa_0''' b^2}{(n_1 - n_2)^2} \frac{(\rho_1 - \rho_2)^2}{m^2} (\Sigma \sqrt{m_1})^2,$$

and therefore

$$\lambda = \left\{ \frac{\kappa'''}{\kappa_0'''} \left( \frac{n_1 - n_2}{b} \right)^2 \right\} \lambda_0 = \mu \lambda_0,$$

where  $\mu$  is the same for all liquids at corresponding states. Another value for  $\mu$  may be obtained from one of the infinite number of subsidiary surface tension relations that can be found. Let us take the modified relation of Eötvös given in this paper. At the absolute zero this becomes

$$\lambda_0 = k \frac{b^{2/3} \rho_c^{2/3}}{m^{2/3}} T_c = \frac{k b^{2/3}}{(n_1 - n_2)^{2/3} (1 - \alpha n_3)} \frac{(\rho_1 - \rho_2)^{2/3}}{m^{2/3}} (T_c - \alpha T),$$

and we therefore deduce

$$\lambda = \mu \lambda_0 = \left\{ \frac{k}{b^{2/3}} (n_1 - n_2)^{2/3} (1 - \alpha n_3) \right\} \lambda_0.$$

\* Phil. Mag. Oct. 1910, pp. 491-510.

† Phil. Mag. May 1910, p. 793.

On equating the two values of  $\mu$  indicated we obtain an expression for  $\kappa'''$ .

An infinite number of expressions for  $\kappa'''$  can thus be obtained; and we cannot therefore determine the form of the arbitrary function in the law of attraction from one of them. This remark applies also to the other constants that will be considered.

The general equation for the internal heat of evaporation deduced from the law of attraction between molecules is

$$L = \left\{ A_1 \left( \frac{\rho_1}{m} \right)^{4/3} - A_2 \left( \frac{\rho_2}{m} \right)^{4/3} \right\} \frac{(\Sigma \sqrt{m_1})^2}{m}, \quad (4)$$

where  $A_1$  and  $A_2$  are each the same for all liquids at corresponding states\*. At the absolute zero this equation becomes

$$\begin{aligned} L_0 &= (A_0' n_1^{4/3} - A_0'' n_2^{4/3}) \frac{b^{4/3} \rho_c^{4/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2 \\ &= (A_0' - A_0'' \frac{n_2^{4/3}}{n_1^{4/3}}) \frac{b^{4/3} \rho_1^{4/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2, \end{aligned}$$

where  $A_0'$  is the value of  $A_1$  and  $A_0''$  that of  $A_2$  at the absolute zero. Since the first of the above equations may be written

$$L = \left( A_1 - A_2 \frac{n_2^{4/3}}{n_1^{4/3}} \right) \frac{\rho_1^{4/3}}{m^{7/3}} (\Sigma \sqrt{m_1})^2,$$

we have

$$L = L_0 \frac{(A_1 n_1^{4/3} - A_2 n_2^{4/3})}{(A_0' n_1^{4/3} - A_0'' n_2^{4/3}) b^{4/3}} = \eta L_0,$$

where  $\eta$  is the same for all liquids at corresponding temperatures. To obtain another value for  $\eta$  let us take the equation

$$L = C(\rho_1^2 - \rho_2^2),$$

where  $C$  depends only on the nature of the liquid†. At the absolute zero we then have

$$L_0 = C \rho_c^2 b^2 = C \frac{b^2(\rho_1^2 - \rho_2^2)}{n_1^2 - n_2^2},$$

and therefore

$$L = \frac{(n_1^2 - n_2^2)}{b^2} L_0 = \eta L_0.$$

On equating these two expressions for  $\eta$  an expression for

$$\left( A_1 - A_2 \frac{n_2^{4/3}}{n_1^{4/3}} \right)$$

in terms of  $n_1$  and  $n_2$  is obtained.

\* Phil. Mag. May 1910, pp. 794-795.

† Phil. Mag. Oct. 1910, p. 678.

From thermodynamics and the law of attraction we obtain

$$T = H^2 \left( \frac{\rho_1}{m} \right)^{4/3} (\Sigma \sqrt{m_1})^2, \dots \dots \dots (5)$$

where  $H^2$  has the same value for all liquids at corresponding temperatures\*. At the critical point the equation becomes

$$T_c = H_c^2 \left( \frac{\rho_c}{m} \right)^{4/3} (\Sigma \sqrt{m_1})^2 = \frac{H_c^2}{n_1^{4/3}} \left( \frac{\rho_1}{m} \right)^{4/3} (\Sigma \sqrt{m_1})^2,$$

and therefore

$$T = \left( \frac{H^2 n_1^{4/3}}{H_c^2} \right) T_c = n_3 T_c,$$

and

$$H^2 = \frac{n_3 H_c^2}{n_1^{4/3}}.$$

Equation (5) was proved for low temperatures, but it will be easily seen that if it holds for one corresponding temperature of a number of liquids it will hold for all temperatures, and the value of  $H^2$  is that given above.

From thermodynamics and the law of attraction we also have

$$p = M^2 \left( \frac{\rho}{m} \right)^{7/3} (\Sigma \sqrt{m_1})^2, \dots \dots \dots (6)$$

where  $M^2$  is the same for all liquids at corresponding temperatures†. At the critical temperature this equation becomes

$$p_c = M_c^2 \left( \frac{\rho_c}{m} \right)^{7/3} (\Sigma \sqrt{m_1})^2 = \frac{M_c^2}{n_1^{7/3}} \left( \frac{\rho_1}{m} \right)^{7/3} (\Sigma \sqrt{m_1})^2,$$

and therefore

$$M_2 = \frac{n_4 M_c^2}{n_1^{7/3}}.$$

The values of the quantities  $n_1$ ,  $n_2$ ,  $n_3$  and  $n_4$ , in the above equations, may be expressed in terms of one of them along the lines indicated in a previous paper‡ and in this paper.

*The Law of Attraction between Molecules stated in  
a more General Form.*

The law of attraction given at the beginning of the paper we would expect on account of its generality to represent the facts only approximately in some cases. We have seen in

\* Phil. Mag. Oct. 1909, p. 509; and May 1910, p. 787.

† Phil. Mag. Dec. 1909, p. 903; and May 1910, p. 788.

‡ Phil. Mag. March 1911, p. 325.

previous papers that a better agreement with the facts is often obtained by using  $\Sigma C_a$  instead of  $\Sigma \sqrt{m_1}$ , the values  $C_a$  being deduced from the experimental data. But the values of  $C_a$  thus found differ little from those of  $\sqrt{m_1}$ . It appears therefore that  $\Sigma \sqrt{m_1}$  should strictly be written  $\Sigma \sqrt{\alpha m_1}$ , where  $\alpha$  denotes a constant depending on the nature of the atom. A better agreement of the law of attraction with the facts would obviously now be obtained on deducing the average values of  $\alpha$  corresponding to each atom from all the available data. But it is probable that a still better agreement would be obtained by dealing with substances in groups, for it is very probable that the values of  $\alpha$  are constant for the atoms of substances belonging to the same chemical group, but differ from group to group, or generally that the properties of  $\alpha$  run parallel with the purely chemical properties of the substances.

The fifth power of  $z$  in the law might perhaps in some cases be replaced by some other power giving a better agreement with the facts. But the application of the law to the facts shows that the modified powers of  $z$  would differ very little from the fifth.

The form of the arbitrary function in the law very probably also depends somewhat on the nature of the substances under consideration. Since the law of corresponding states follows if the function is one of the ratios  $\frac{T}{T_c}$  and  $\frac{z}{x_c}$ , and is the same for all substances \*, a deviation from the law would indicate a change in the form of the arbitrary function. It will very probably be found when sufficient reliable data for comparison are available, that the substances which have a very low critical temperature do not fit in very well with the other substances in respect to the law of corresponding states.

A more general expression for the law of attraction between two molecules is therefore

$$\psi \phi_2 \left( \frac{T}{T_c}, \frac{z}{x_c} \right) \cdot \frac{(\Sigma \sqrt{\alpha m_1})^2}{z^{\gamma^5}},$$

where  $\alpha$ ,  $\gamma$ , and  $\psi$  are quantities which depend to a certain extent on the nature of the substance under consideration, but which as a rule differ very little from unity. The quantities  $\alpha$ ,  $\gamma$ , and  $\psi$  are probably each the same for each group of substances possessing similar chemical properties, and otherwise are intimately connected with the chemical constitution of substances.

It should be observed that when a good agreement of the

\* Phil. Mag. March 1911, pp. 336-341.

formulæ deduced from the law of attraction is not obtained, this may be due in some cases to the molecules of the substance under consideration being polymerized, and the necessary factors of the molecular weight, etc., taking this into account not having been introduced.

*The Fundamental Relations.*

Traube\* has shown that the molecular volume of a molecule in a liquid at the absolute zero is proportional to  $\Sigma \sqrt{m_1}$ . The molecular volume at any temperature of a liquid may therefore, according to the law of corresponding states, be written

$$\frac{m}{\rho_1} = \frac{u}{n_1} \Sigma \sqrt{m_1}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where  $u$  is a universal constant. If we substitute for  $\frac{\rho_1}{m}$  in equations (3) (4) (5) (6) from equation (7) we obtain expressions for  $T, p, L$ , and  $\lambda$ , in terms of  $m_1, n_1, n_2, n_3$ , and  $n_4$ , and  $T_c, p_c, \lambda_0, L_0$ , in terms of  $m_1$ . This shows that we need not look for any further fundamental relations connecting the above quantities than the equations (3), (4), (5), (6), (7), for we could not expect the expression for the critical constants of a substance to involve fewer and more fundamental quantities than the atomic weights of a molecule. Equation (7) expresses an independent fundamental law, and equations (3), (4), (5) and (6) are obtained from the law of attraction between molecules given at the beginning of the paper and the laws of thermodynamics. But it is found that the equations obtained on making the above substitution agree only roughly with the facts. This is due partly to the law of Traube being only approximately true, strictly it should be written

$$\frac{m}{\rho_1} = \frac{u}{n_1} \Sigma \sqrt{\beta m_1},$$

where  $\beta$  is a constant which depends probably on the constitution of the molecule. If the more general law of attraction is used in deducing equations (3), (4), (5) and (6), and  $\alpha$  and  $\beta$  are determined from some of the experimental data, a much better agreement with the facts is at once obtained. The values of  $\rho_c, T_c$ , and  $p_c$  would then for example be proportional to

$$\frac{m}{\Sigma \sqrt{\beta m_1}}, \quad \frac{(\Sigma \sqrt{\alpha m_1})^2}{(\Sigma \sqrt{\beta m_1})^{4/3}}, \quad \text{and} \quad \frac{(\Sigma \sqrt{\alpha m_1})^2}{(\Sigma \sqrt{\beta m_1})^{7/3}},$$

respectively.

\* *Phys. Zeit.* Oct. 1909, p. 667.



*Other Relations.*

The equations (3), (4), (5), (6), and (7) are the fundamental equations giving the relations between the quantities which they contain, and it should therefore be possible to reduce all other empirical relations between these quantities to one of these equations. We will illustrate this by some examples.

Walden\* has shown that the expression  $\frac{m\lambda}{\rho_1 \Sigma v}$  is equal to the same constant for all liquids at their boiling-points, where  $\Sigma v$  is the sum of the maximum valencies of the atoms of a molecule. Substituting for  $\lambda$  in this expression from equation (3), and  $\Sigma \sqrt{m_1}$  for  $\Sigma v$ , since these quantities are approximately equal to one another †, we obtain, since the boiling-points are approximately corresponding points, that  $\frac{\rho_1 \Sigma \sqrt{m_1}}{m}$  is a constant. This, it will be seen, is Traube's law.

Walden also showed that  $\frac{L\rho}{m\lambda}$  is constant at the boiling-point, where  $L$  is the (total) heat of evaporation. Now the work done during evaporation is the same fraction of the internal heat of evaporation for all liquids at corresponding temperatures (see "Heat of Evaporation," this paper), and we may therefore substitute for  $L$  from equation (4), and substituting for  $\lambda$  as before the expression becomes  $\left(\frac{\rho_1}{m}\right)^{1/3}$ . Now this is approximately constant as  $\frac{\rho_1}{m}$  does not vary much with the nature of the liquid. To conform to equations (3) and (4) the above expression should be written  $\frac{L\rho_1^{2/3}}{\lambda m^{2/3}}$ , when it will at once reduce to a constant on substituting for  $\lambda$  and  $L$ .

Walden states in his paper that  $\frac{T}{\Sigma v}$  is equal to the same constant for all liquids at their boiling-points. But this happens to apply only to the liquids mentioned in his paper. The quantity is found to be by no means constant when all the available data are considered. Its properties have been discussed in a paper by the writer ‡, in which a meaning of its constancy in the case of some liquids will be found.

\* *Zeit. für phys. Chemie*, vol. lxx. 1908-1909, pp. 257-261.

† *Phys. Zeit.* Oct. 1909, p. 667; *Phil. Mag.* May 1910, pp. 784-788.

‡ *Phil. Mag.* Dec. 1910, p. 905.

*Deductions from the Law of Molecular Attraction.*

Further results will now be obtained depending on the general law of attraction given at the beginning of the paper. Substituting the value of  $L$  from equation (4) in Clapeyron's equation we obtain for the limiting form of the equation at the critical point

$$\begin{aligned} T_c \left( \frac{dp}{dT} \right)_c &= p_c + (\Sigma \sqrt{m_1})^2 A \left( \frac{\rho_c^{4/3}}{m^{7/3}} \right) \left( \frac{1-yx^{4/3}}{1/x-1} \right) \text{Lt}_{\substack{x=1 \\ y=1}} \\ &= p_c + A_c \frac{\rho_c^{4/3}}{m^{7/3}} \frac{7}{3} (\Sigma \sqrt{m_1})^2, \end{aligned}$$

where we have put  $A_1 = yA_2$ ,  $\rho_2 = x\rho_1$ , and  $A_c$ —a universal constant—for the limiting value of  $A_1$ . By means of equation (6) the above equation becomes

$$\left( \frac{dp}{dT} \right)_c = \frac{p_c}{T_c} \left( 1 - \frac{A_c}{M_c^2} \frac{7}{3} \right) = \frac{p_c}{T_c} \cdot W_c \text{ say,}$$

where  $M_c^2$  is a universal constant. The value of  $W_c$  may be expressed in a more convenient form. Equating the value of  $L$  given by the fundamental equation (4) with that given by the equation

$$L = \frac{K_4 RT}{m} \log \left( \frac{\rho_1}{\rho_2} \right)$$

(one of the infinite number of subsidiary equations that can be obtained for the heat of evaporation), we obtain for the limiting value of  $A_1$  the expression

$$\frac{RK_4 T_c m^{4/3}}{(\Sigma \sqrt{m_1})^2 \rho_c^{4/3}} \frac{3}{7}.$$

By means of equation (5) this becomes

$$H_c^2 RK_4 \frac{3}{7},$$

where  $H_c^2$  is a universal constant, and therefore we have

$$W_c = \left( 1 + \frac{H_c^2 K_4}{M_c^2} \right).$$

Now from equations (5) and (6) we have

$$p_c = \frac{M_c^2}{H_c^2} \frac{\rho_c T_c}{m}.$$

This equation applied to the facts gives

$$p_c = \frac{R \rho_c T_c}{m \cdot 3 \cdot 7}$$

(Young and Thomas' law), and therefore

$$\frac{H_c^2}{M_c^2} = 3.7.$$

The value of  $W_c$  thus becomes  $(1 + 3.7K_4)$ , and since  $K_4 = 1.75$  we obtain finally

$$\left(\frac{dp}{dT}\right)_c = \frac{p_c}{T_c} 7.5.$$

The above equation has already been put forward as an empirical relation by Dieterici \*, who finds that

$$\left(\frac{dp}{dT}\right)_c = \frac{2R}{m} \rho_c,$$

which may be written

$$\left(\frac{dp}{dT}\right)_c = \frac{p_c}{T_c} 7.4,$$

and thus agrees well with the equation deduced theoretically.

The value of  $\frac{dL}{dT}$  at the critical point may be obtained from the law of attraction between molecules. From equation (4) we have

$$\frac{dL}{dT} = \left(\sum \sqrt{\overline{m_1}}\right)^2 \left\{ \frac{dA_1}{dT} \rho_1^{4.3} - \frac{dA_2}{dT} \rho_2^{4.3} + \frac{A_1 4 \rho_1^{1/3}}{3} \frac{d\rho_1}{dT} - \frac{A_2 4 \rho_2^{1/3}}{3} \frac{d\rho_2}{dT} \right\}.$$

Now

$$A_1 = \phi_3\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_1}\right) = \phi_3\left(n_3, \frac{1}{n_1}\right),$$

and

$$A_2 = \phi_3\left(\frac{T}{T_c}, \frac{\rho_c}{\rho_2}\right) = \phi_3\left(n_3, \frac{1}{n_2}\right),$$

and therefore

$$\frac{dA_1}{dT} = \frac{d\phi_3}{dn_3} \frac{1}{T_c} - \frac{d\phi_3}{dn_1} \frac{\rho_c}{\rho_1^2} \frac{d\rho_1}{dT},$$

and

$$\frac{dA_2}{dT} = \frac{d\phi_3}{dn_3} \frac{1}{T_c} - \frac{d\phi_3}{dn_2} \frac{\rho_c}{\rho_2^2} \frac{d\rho_2}{dT}.$$

From thermodynamics we have

$$\frac{d\rho_1}{dT} = - \frac{d\rho_2}{dT} = \infty$$

at the critical point. It will now be easily seen that at the critical point

$$\frac{dL}{dT} = \infty.$$

\* *Ann. der Physik*, vol. xii. 1903, p. 144.

*Consequences of an Even Distribution of Matter in Space.*

In previous papers the writer\* has deduced formulæ on the supposition that matter does not consist of molecules but is evenly distributed in space. On making the additional supposition that the internal heat of evaporation consists only of the work done against the attraction of the elements of matter upon one another, it was shown, for example, that  $L_1\rho_1 = P'_{n_1}$ , where  $P_{n_1}$  is the intrinsic pressure of the liquid and  $L_1$  the internal heat of evaporation of unit mass into a vacuum. At low temperatures, when the density of the vapour is small in comparison with that of the liquid,  $L_1$  is the ordinary heat of evaporation. The result is independent of the law of attraction between the elements of matter. The subject will be extended in this paper.

From the above result it follows that the heat of evaporation is given by the expression  $\left(\frac{P_{n_1}}{\rho_1} - \frac{P_{n_2}}{\rho_2}\right)$ , where  $P_{n_2}$  denotes the intrinsic pressure of the saturated vapour and  $\rho_2$  its density. If we put  $P_{n_2} = xP_{n_1}$  and substitute the above expression in Clapeyron's equation we obtain

$$P_{n_1}\left(\frac{1}{\rho_1} - \frac{x}{\rho_2}\right) = \left(\frac{1}{\rho_2} - \frac{1}{\rho_1}\right)\left(T\frac{dp}{dT} - p\right).$$

At the critical point  $x$  becomes equal to unity and the equation becomes  $P_{nc} = p_c - T_c\frac{dp}{dT}$ , where  $P_{nc}$  denotes the intrinsic pressure at the critical point. Now we have seen in a previous part of the paper that at the critical point

$$T_c\frac{dp}{dT} = 7.5 p_c,$$

and thus  $P_{nc} = -6.5 p_c$ .

The above expression for the intrinsic pressure may be written in a different form. The attraction between two elements of matter  $dz$  may be written  $\rho^2 W(dz)^2 \cdot \phi(x, T)$ , where  $x$  is the distance of separation of the elements,  $\rho$  the density of the matter, and  $W$  a constant depending on its nature. The expression for the internal heat of evaporation given in a previous paper† now becomes  $WK\rho$ , where  $K$  is the same for all matter. If  $K$  is constant, that is, if the attraction does not depend on the temperature, the intrinsic pressure may be written  $Z\rho^2$ , where  $Z$  depends only on the nature of the liquid. Now the intrinsic pressures

\* Phil. Mag. June 1910, p. 840, and Oct. p. 665.

† Loc. cit.

obtained from the preceding expressions very nearly obey this law. Thus the values of the intrinsic pressures in atmospheres for ether at the temperatures  $273^{\circ}$  and  $373^{\circ}$ , given by the expression  $L_1\rho_1$ , are 2664 and 1546, while the value at the critical point is 235.8. The ratio of these values to the corresponding values of  $\rho_1^2$  are 4916, 4148, and 3472, respectively, and thus approximately constant. Thus although matter consists of molecules, a liquid behaves approximately as if the matter were evenly distributed in space, and the attraction independent of the temperature.

Since the density of a liquid at the absolute zero is about 4 times that at the critical temperature, the intrinsic pressure in the former case is about 16 times that in the latter.

It is of interest that the intrinsic pressure term in Van der Waals' equation of state is of the same form as the above, and thus corresponds to an even distribution of matter in space.

A better agreement of the above expression with the facts is obtained by writing  $\rho^{2.33}$  instead of  $\rho^2$ . Since the intrinsic pressure is for all liquids at corresponding states the same multiple of the critical pressures, its general equation must take the form

$$P_n = A \left( \frac{\rho}{\rho_c} \right)^{2.33} p_c.$$

The value of A when  $P_n$  is expressed in atmospheres is 6.52.

Since  $L_1 = WK\rho_1$  in the case of a liquid, we have  $L_2 = WK\rho_2$  in the case of its saturated vapour, and therefore  $\frac{L_1}{L_2} = \frac{\rho_1}{\rho_2}$ . From Clapeyron's equation we have

$$L_1 - L_2 = \left( T \frac{dp}{dT} - p \right) \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right),$$

and hence

$$L_1 = \frac{1}{\rho_2} \left( T \frac{dp}{dT} - p \right), \text{ and } L_2 = \frac{1}{\rho_1} \left( T \frac{dp}{dT} - p \right),$$

since the ratio  $\frac{L_1}{L_2}$  from these equations is the same as that given by the above equation. These equations must hold if matter is evenly distributed in space; from what has gone before we would expect them to agree approximately with the facts.

They afford a test sometimes whether matter is evenly distributed in space. For example, the values of  $\rho_2$  and  $p$  for the vapour of water at zero are the same as for the

vapour of ice, but  $\frac{dp}{dT}$  is larger and  $L_1$  smaller in the case of ice than in the case of water. The equations cannot therefore agree with the facts in each case, which indicates that the matter is not evenly distributed in space in one or both cases.

Cambridge, March 10th, 1911.

LIV. *Production of Helium by Radium.* By Prof. B. B. BOLTWOOD and Prof. E. RUTHERFORD, F.R.S.\*

*Introduction.*

THE connexion of helium with the transformation of radioactive material has been a problem of great interest and importance for the past eight years, and has been the subject of a number of investigations.

In 1908, Rutherford and Soddy † advanced the theory of the disintegration of radioactive matter and suggested that the helium, which occurs in such relatively large quantities in radioactive minerals, was probably one of the products of transformation of the radio-elements contained in these minerals. In 1903, Ramsay and Soddy ‡ showed experimentally that helium could be obtained from a salt of radium and that helium was produced from the emanation of radium. In these early experiments, the helium was present in minute quantity and was detected by spectroscopic tests. These observations were shortly afterwards confirmed by a number of independent experimenters. Somewhat later Debierne found that helium was produced also from preparations of actinium.

At the time of the discovery of the production of helium by radium, it was of fundamental importance to fix the position of helium in the general scheme of radioactive transformations. In 1903, Rutherford § showed that the  $\alpha$  rays emitted by radium consisted of positively charged particles moving with a high velocity. The determination of  $e/m$ —the ratio of the charge to the mass of the  $\alpha$  particle—indicated that the  $\alpha$  particle was of atomic dimensions and of apparent mass about twice that of the hydrogen atom.

\* A preliminary note on the subject was communicated by the Authors to the Manch. Lit. and Phil. Soc. No. 6, 1909. The complete paper was published in the *Wiener Berichte*, cxx. II. a, March 1911.

† Phil. Mag. [6] vol. iv. p. 582 (1902).

‡ Proc. Roy. Soc. vol. lxxii. p. 204 (1903).

§ Phil. Mag. [6] vol. v. p. 177 (1903).

From the beginning it seemed probable that, if the  $\alpha$  particles consisted of any known kind of matter, they must either be charged molecules of hydrogen or charged atoms of helium; and Rutherford \* had pointed out, immediately after the production of helium from radium had been experimentally demonstrated, that the source of the helium was in all probability the accumulated  $\alpha$  particles expelled from radium and its products. On this hypothesis, making use of the imperfect data available at that time, an estimate was made of the rate of production of helium by one gram of radium in equilibrium, which indicated that the amount of helium produced per year should be between 20 and 200 cubic millimetres.

The importance of determining the true nature of the  $\alpha$  particles led to a more accurate measurement of the velocities and the values of  $e/m$  of the  $\alpha$  particles expelled from the different types of active matter. The value of  $e/m$  was found to be 5070 electromagnetic units †.

The results indicated that the  $\alpha$  particle was either a hydrogen molecule carrying a single ionic charge or a helium atom carrying two ionic charges (the latter possibility being considered the more probable), and suggested that helium was a product of transformation of all types of radioactive matter emitting  $\alpha$ -rays.

The question was further investigated by Rutherford and Geiger ‡, who developed a method of directly counting the  $\alpha$  particles emitted by a radioactive substance. It was found § that one gram of radium itself emitted  $3.4 \times 10^{10}$   $\alpha$  particles per second and that radium in equilibrium with its three  $\alpha$ -ray products emitted four times this number. At the same time the charge carried by each  $\alpha$  particle was found to be  $9.3 \times 10^{-10}$  electrostatic unit. From the various evidence, it was concluded that the  $\alpha$  particles did carry two unit charges, and that the value of the unit charge, *i. e.* the charge carried by the hydrogen atom, was  $4.65 \times 10^{-10}$  electrostatic unit. The final proof of the connexion of the  $\alpha$  particles with the helium atom was supplied by Rutherford and Royds ||, who showed that helium always accumulated when  $\alpha$  particles were allowed to penetrate into vacuous space or into solid matter. It was thus definitely proved

\* Nature, vol. lxviii. p. 366 (1903).

† Rutherford, Phil. Mag. vol. xii. p. 358 (1906).

‡ Proc. Roy. Soc. vol. lxxxi. p. 151 (1908).

§ Proc. Roy. Soc. vol. lxxxii. p. 162 (1908).

|| Phil. Mag. vol. xvii. p. 281 (1909).

that the  $\alpha$  particle is a projected atom of helium which carries two unit charges.

Rutherford and Geiger\* calculated the rate of production of helium by radium to be expected on the basis of the above data. One gram of radium in equilibrium expels  $13.6 \times 10^{10}$   $\alpha$  particles, *i.e.* atoms of helium, per second. Taking the charge carried by the hydrogen atom as  $4.65 \times 10^{-10}$ , it can at once be calculated from the electrochemical equivalent of hydrogen that one cubic centimetre of any gas at standard pressure and temperature contains  $2.72 \times 10^{19}$  molecules. As helium is monatomic, the rate of production of helium per gram of radium is  $\frac{13.6 \times 10^{10}}{2.72 \times 10^{19}}$  c.c. per second, or 158 cubic millimetres per year.

The first direct determination of the rate of production of helium by radium was made by Sir James Dewar†, using 70 milligrams of anhydrous chloride—part of the material prepared by Dr. Thorpe for the determination of the atomic weight of radium. The radium salt in the crystalline state was contained in an exhausted vessel connected with a MacLeod gauge. The salt was occasionally heated to drive off the accumulated helium, and other gases which might be present were removed by exposure to a small fragment of coconut charcoal cooled by liquid air. An estimate of the amount of hydrogen present in the gaseous mixture was obtained by further cooling the charcoal to the temperature of liquid hydrogen.

In the first paper published it was concluded that one gram of radium in equilibrium produced 0.37 cubic millimetre of helium per day. In a later experiment‡ the radium was sealed up for a period of nine months, and the average rate of production of helium was estimated to correspond to 0.463 cubic millimetres per day. It was pointed out in the second paper that when the results of the first experiment were corrected for an error in the original calculation, the rate of the production of helium in the first experiment corresponded to 0.499 instead of 0.37 cubic millimetre per day per gram of radium. The rate of the production of helium per gram of radium per year indicated by these experiments is therefore 182 cubic millimetres in the first and 169 cubic millimetres in the second. These values are both somewhat higher than the calculated quantity, *viz.* 158 cubic millimetres.

\* Proc. Roy. Soc. vol. lxxxi. p. 162 (1908).

† Proc. Roy. Soc. vol. lxxxi. p. 280 (1908).

‡ Proc. Roy. Soc. vol. lxxxiii. p. 404 (1910).



Since it is important that the rate of production of helium by radium should be known as accurately as possible, an independent determination of this magnitude has been carried out by the writers. Two separate determinations of the rate of production of helium have been made, using for the purpose a considerable portion of the specimen of radium salt kindly loaned to one of the writers by the Vienna Academy of Sciences.

### *Preparation of Material.*

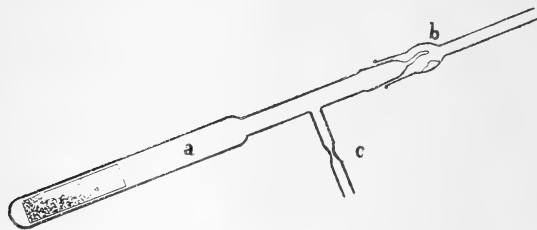
It was quite essential that the radium salt used in these experiments should be relatively free from radioactive substances other than radium. The salt consisted of a quantity of barium-radium chloride, containing about 7 per cent. of the latter element, and before it came into our hands had been originally subjected to a partial fractional recrystallization. It was therefore highly improbable that radioactive substances other than radium and the disintegration products of radium were present. The salt had been preserved in a slightly acid, aqueous solution for a period of over a year previous to the time when these experiments were begun, and had existed in the form of a crystalline salt for a somewhat indefinite period before this. In order to remove the radio-lead and polonium which had accumulated during this interval the solution was treated as follows:—About fifty milligrams of antimony trichloride, ten milligrams of lead nitrate, and five milligrams of bismuth nitrate were dissolved in a small quantity of dilute hydrochloric acid, and this solution was added to the solution of the radium salt. The mixture was diluted with water to a volume of about 100 c.c. and an excess of hydrogen sulphide was run in. Because of the addition of the antimony salt, the precipitate of sulphides coagulated and could be readily removed by filtration through paper, after which it was well washed with distilled water. The precipitate on the paper was decomposed by warming with dilute hydrochloric acid to which a few small crystals of potassium chlorate had been added, and, after diluting with water, the treatment with hydrogen sulphide was repeated. The second precipitate of sulphides was filtered off and the filtrate was added to the filtrate from the first operation. The object in adding the lead and bismuth salts to the original solution was to insure the complete separation of the radio-lead and polonium\*.

The combined filtrates from the sulphides were evaporated

\* Boltwood, *American Journal of Science*, vol. xxv. p. 228 (1908).

to dryness in a silica dish on a water-bath and the residue of radium-barium chloride was heated gently to remove the excess of hydrochloric acid and water. The dry salt was then placed in a cylindrical platinum capsule which was closed by a perforated cover. The capsule was next sealed up in a tube of Jena "combustion" glass (*a*, fig. 1). One

Fig. 1.



end of this tube was ground to fit into a tube of soft glass *b* and the extremity of the tube *a*, extending into the joint at *b*, terminated in a slightly curved, narrow, closed, capillary tube. An inward depression in the tube *b* near the joint made it possible, by rotating the tube *a* in the joint *b*, to break off the capillary extension of *a* and thus establish communication between *a* and *b* when desired. This arrangement was designed to facilitate the removal of the helium at the end of the period of accumulation. The Jena glass tube was completely exhausted of air through the tube *c*, which was then sealed off.

#### *Determination of Radium in Salt.*

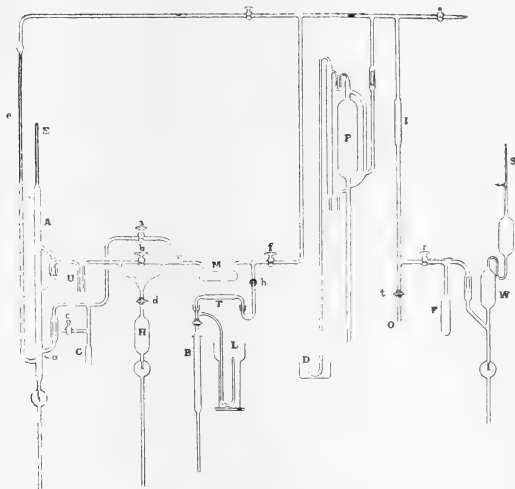
The amount of radium present in the salt contained in the capsule was determined by the measurement of the  $\gamma$  radiation emitted after a period of over two months from the time of sealing up the tube. Using a thick-walled, lead electroscope, the  $\gamma$  ray activity of the salt in the tube was compared with the  $\gamma$  ray activity of the 3.69 milligram radium bromide standard of this Laboratory both directly and by a comparison with a third specimen of radium salt containing approximately 32 milligrams of radium bromide calibrated in terms of the small standard. The comparisons of the radium quantities were made at various distances and under different conditions, and gave the amount of radium in the salt used in the experiment as 191 milligrams (equivalent to 326 milligrams of radium bromide).

When the experiments on the determination of the production of helium had been completed a further measurement of the amount of radium present in the salt used was made as follows:—The salt was dissolved in distilled water containing a small quantity of hydrochloric acid and the solution was diluted to a definite volume (50 c.c.). A small, definite fraction (1.22 per cent.) of this solution was removed, evaporated to dryness in a small glass tube, and hermetically sealed by fusing the glass. After a month's time the small fraction was directly compared by means of the  $\gamma$  radiation with the 3.69 milligram radium bromide standard of this Laboratory, and found to be equivalent to 4.02 milligrams  $\text{RaBr}_2$ . The results of this comparison gave the amount of radium present in the salt used as 193 milligrams.

*Collection and Measurement of the Helium.*

The helium produced by the radium salt was collected, purified, and measured in the apparatus shown in fig. 2.

Fig. 2.



This consisted of a Giessler pump, P, which was used for the evacuation of the other portions of the apparatus. The gases removed by this pump could be collected when desired at D. The vessel M contained phosphorus pentoxide for the removal of water vapour. The vessel A with the attached capillary tubes E and e was essentially a MacLeod gauge in its design and operation, but in these experiments was used for the

measurement of volumes rather than of pressures as is the usual method of employing this type of apparatus. The volume of the capillary tube E was accurately determined for various lengths by direct calibration with a thread of mercury. The comparison tube *e* was made from the same piece of tubing as E and had essentially the same diameter and cross-section of bore, so that no correction had to be made for the capillary depression of the mercury in the tube E when the pressure of gas contained in E was measured. Two side tubes entering the tube A from the right could be closed by glass float-valves, the lower of the usual design, the upper of a special design, which prevented the "trapping" of gas between the glass float and outer jacket. The lower tube extended to the phosphorus pentoxide bulb M, was provided with a stop-cock *a*, and connected with the carbon tube C, which contained a few grams of coconut charcoal. A side tube *c* permitted the introduction of small volumes of pure, dry, electrolytic oxygen at this point in the apparatus. The upper of the two tubes leading from A to the right had a thin-walled bend, U, and led through the stop-cock *b* to the tube M and through the stop-cock *d* to the transfer pump H. The transfer pump H was used for removing gas from the bulb M and introducing it into A and its connexions.

Further attachments to this portion of the apparatus consisted of the burette B with sealed-in platinum wires between which a spark could be produced. This burette was used for introducing gases into the apparatus by way of the tube L which terminated under mercury. After sparking, the gases could be passed through the tube T, of hard glass, containing copper oxide heated to a red heat.

The remaining portion of the apparatus, shown on the right, was used for examining the spectrum of the gas which had been measured in A. The details of its construction will not be described in this paper, but it is sufficient to say that it permitted the removal of the residual gas from the tube A, and its introduction into the small tube S where its spectrum could be conveniently examined.

All of the different vessels, A, H, B, &c. were provided with Bunsen traps to prevent the entrance of air along the mercury columns, and the glass tubes connected with these extended downwards for a distance of over 76 cms. as is the usual practice. The extension of these tubes, the rubber tubes, and the mercury reservoirs attached to the lower ends are not shown in the diagram.

*Calibration of Measuring Portion of Apparatus.*

As already explained the vessel A was in its general design similar to an ordinary MacLeod gauge. For the purposes of the experiments, it was calibrated in the following manner. The entire apparatus was completely freed from air, the vessel C being heated to a low red heat to remove the gases absorbed in the coconut charcoal, and the pressure in the apparatus was reduced to a very low one by continued pumping with the large pump P. The level of the mercury in A was raised to the point *a*, the stop-cocks *f*, *d*, *a*, and *c* were closed, and a small quantity of oxygen mixed with pure helium (obtained from a crystalline uraninite) was introduced into A through the tube L and its connexions. The stop-cock *b* was now closed and the liquid air was placed around the tube C. After about twenty minutes the mercury was raised in A and the volume and pressure of gas in the capillary tube E was measured. With the mercury still raised to the top of A, the stop-cocks *a*, *b*, and *f* were opened, the liquid air was removed from around C, which was allowed to warm up and was finally heated to a low red heat, and the tubes C, U, M, &c. were pumped out thoroughly. The stop-cocks *a* and *b* were now closed, liquid air was placed around C and U, and the mercury in A was lowered to the point *a*. This permitted the helium which had been previously trapped in E to expand into the tubes U and C. The mercury was again raised in A and the volume of helium in E was measured. The ratio of the volume of helium in E in the second measurement to the volume of helium in E in the first, was the ratio of the amount of helium trapped in E, on raising the mercury in A, to the total volume of helium contained in A and its connexions. With the mercury still raised in A, the other tubes were again pumped out and the expansion of the helium in E into the connected tubes U, C, was again repeated. Several operations were carried out in this manner giving results in excellent agreement with one another, and indicating that 71.5 per cent. of the total volume of helium in the apparatus was trapped in the tube E when the mercury in A was raised under standard conditions.

By pumping out the tube A and its connexions to the highest possible vacuum obtainable by the use of the pump P, closing the stop-cocks *a*, *b*, *c*, and immersing the tube C in liquid air for twenty minutes or more, it was possible to obtain so low a vacuum in the tube A that, on raising the mercury in A, no measurable increase of pressure in E was indicated when the mercury was raised in E to within a

millimetre of the closed end. Under these conditions, by a long series of comparisons, it was possible to correct the readings in *E* and *e* for any slight differences due to small irregularities in the bore of *E* and *e*. It was determined, in this manner, that when the tube *E* contained gas, the pressure of the gas, indicated by the relative heights of the mercury columns in *E* and *e*, could be accurately estimated to within less than 0.5 mm. of mercury.

### *Helium from Radium Salt.*

#### (First Determination.)

The barium-radium salt (page 589) still containing a portion of its water of crystallization was sealed up in the tube described on page 590 (fig. 1) for eighty-three days. A small bulb containing  $P_2O_5$  and another containing solid KOH were sealed on to the apparatus (fig. 2) at the point O. The tube *b* (fig. 1) was attached to the KOH tube, the radium tube *a* (fig. 1) was inserted in this, and the entire apparatus was evacuated down to the joint of *a* and *b* (fig. 1). Stop-cocks *r* and *f* were closed. The capillary tip of the radium tube was broken off in the joint *b* and the gases in the radium tube were pumped out and collected at D (fig. 2). During the pumping process, the lower end of the radium tube and the platinum capsule were heated to a red heat. The water of crystallization remaining in the salt was driven out and condensed in the KOH and  $P_2O_5$  bulbs. The radium salt was heated for about thirty minutes. A small amount of electrolytic oxygen was added to the gaseous mixture, the gases were introduced into B (fig. 2) through the tube L and sparks were passed between the electrodes. The residual gases were then slowly pumped over into the tube A, through the tube U which was immersed in liquid air. The radium emanation in the gaseous mixture was condensed in the tube U. When the gas had been completely transferred into the tube A, the charcoal tube C was dipped into liquid air, the level of the mercury in A being at the point *a*. After an interval of about twenty minutes, the mercury was raised in A and the volume and pressure of the gas trapped in E was measured. The level of the mercury in A was now lowered to below the opening of U into A, and by means of the transfer pump H, the uncondensed gases in C and its connexions were pumped out and introduced into A through U. With the stop-cocks *b* and *d* closed and the stop-cock *a* opened, the liquid air was removed from the charcoal tube, this was heated, and the gases previously condensed in C

were pumped out through the large pump. The stop-cock *a* was closed, liquid air was again placed around the tube C and the mercury in A was lowered to the point  $\alpha$ . The gases in A were in this manner again exposed to the cooled charcoal, and after an interval of about thirty minutes the mercury was raised in A and the volume and pressure of gas in E was again determined. Following this, the undensified gases in the tube C were transferred into A, the liquid air was removed and the tube C was warmed up. Any gases condensed in C were pumped out through the large pump. This cycle of operation was repeated, a total of five times giving a series of five separate measurements of pressures and volumes. The results of the second and third showed a slight diminution in the values, but the last three were in satisfactory agreement within limits of 1 per cent. and indicated that the purification of the helium had been carried as far as it could be by treatment with the cooled charcoal. The helium in the apparatus was then introduced into the spectrum tube S and its spectrum examined. It was found to be essentially pure helium. In this experiment no other precautions had been taken to remove the hydrogen from the mixture of gases evolved by the radium salt except the sparking of the mixture with oxygen and the exposure of the residual gases to cooled coconut charcoal in the manner just described. The copper-oxide tube T was not attached to the apparatus until after the first determination had been made. As it is well known, from the valuable researches of Sir James Dewar and others, that the treatment with charcoal alone is not efficient in removing the last traces of hydrogen under these conditions, an experiment was carried out to determine to what extent the presence of free hydrogen might have affected the results. A small volume of hydrogen was therefore introduced into the apparatus and put through the same series of operations as had been carried out with the gases obtained from the radium salt. It was found that the gas remaining after the first treatment with cooled charcoal became rapidly less, and after three cycles of exposure decreased to an amount which was under 1 per cent. of the volume of the helium obtained from the radium salt. It seemed improbable, therefore, that any serious error could have arisen on this account.

Another matter which required attention was the question as to whether the helium produced in the radium salt had been completely set free on heating the salt. Before the salt was heated, the tube containing it was carefully examined to determine what proportion, if any, of the radium

emanation escaped from the solid salt and diffused into the upper portion of the tube. A considerable proportion of the  $\alpha$  particles resulting from the disintegration of such free emanation might be expected to embed themselves in the walls of the tube and introduce an error which could not easily be avoided. Measurements of the  $\gamma$  radiation from the upper portion of the tube when the lower portion containing the radium salt was screened by a thick lead block, showed that the amount of emanation in the upper part of the tube was too small to be detected, although as little as 1 per cent. of the total could have been easily observed. It was therefore apparent that the escape of the emanation from the solid salt did not need to be taken into consideration. After the radium salt had been heated, a further series of measurements of the  $\gamma$  radiation was carried out, which indicated that the emanation had been completely separated from the salt by the heating process. It was therefore reasonable to presume that the helium also was quite completely removed at the same time.

#### *Helium from Radium Salt.*

(Second Determination.)

In order to leave no doubt as to the influence of the hydrogen present in the first experiment, and to avoid all possibility of incompleteness in the removal of the helium from the salt, a second determination of helium was made under distinctly different conditions. The tube T containing copper oxide was introduced into the apparatus, and it was found by experiment that the last traces of hydrogen could be removed by passing a mixture of hydrogen with an excess of oxygen through this copper-oxide plug heated to a low red heat.

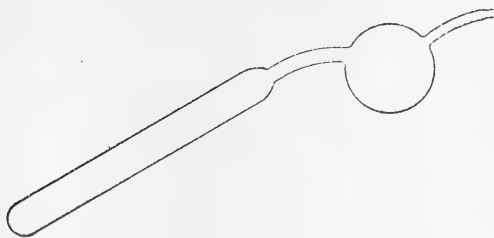
The radium salt was sealed up for a further period of 132 days. At the end of this time the gases, consisting chiefly of oxygen which had been introduced before sealing up the salt, were pumped out and collected. The radium salt was then removed from the glass tube in which it had been sealed, the perforated cover was taken off the platinum capsule, and the capsule was sealed into another glass tube (fig. 3).

The radium capsule was placed in the bottom of the cylindrical tube (fig. 3), the lower portion of this tube was wrapped with wet paper to prevent any heat reaching the



radium salt, and the upper portion of the tube (fig. 3) containing the bulb was sealed on. The object of having the bulb in the upper extremity of this tube was to prevent the escape of the radium solution through excessive boiling later under diminished pressure.

Fig. 3.



This tube was closed at one end by one short piece of thick-walled rubber tubing and a screw pinchcock. The air was completely removed from the tube, and about 30 cubic centimetres of a dilute solution of hydrochloric acid was introduced through the rubber tubing in such a manner as to preclude the admission of any traces of air. The radium salt was now completely dissolved by gentle warming of the tube and the gases were pumped out of this tube, through small KOH and  $P_2O_5$  bulbs, and finally through a thin-walled U tube cooled in liquid air (for removing the radium emanation at this point) attached at O (fig. 2). These gases were combined with the gases previously pumped off and the mixture was introduced into the gas burette B. After passing sparks between the electrodes in B, the gases were drawn through the copper oxide in T (heated to low redness) and introduced into the measuring portion of the apparatus, where the volume of the helium was determined in the manner described under the first determination. The cycle of operations carried out in the measurement of this second quantity of helium comprised three separate exposures to the cooled charcoal, with the removal of any condensed gases from the charcoal after each determination. The results obtained were in excellent agreement and showed no such variations at the start as had been observed in the first experiment, when the removal of the hydrogen had not been complete previous to the introduction of the gases into A.

The results obtained in both determinations were as follows:—

First determination.—Period of accumulation 83 days.

Volume of Helium at 0° and 760 mm. pressure.

First measurement of series	.....	9.08	cubic millimetres.
Second	„ „	6.79	„ „
Third	„ „	6.59	„ „
Fourth	„ „	6.54	„ „
Fifth	„ „	6.60	„ „

Average of third, fourth, and fifth 6.58 „ „

Second determination.—Period of accumulation 132 days.

Volume of Helium at 0° and 760 mm. pressure.

First measurement of series	.....	10.32	cubic millimetres.
Second	„ „	10.37	„ „
Third	„ „	10.45	„ „

Average of all ..... 10.38 cubic millimetres.

#### *Calculation of Rate of Production of Helium.*

If  $x$  is the volume of helium produced per day by the amount of radium (element) present in the salt, and  $y$  is the volume of helium produced per day by the emanation and the two  $\alpha$ -ray products (radium A and radium C) in equilibrium with the radium; then when the three latter products are present in equilibrium amounts  $y=3x$ , or, in other words, the amount of helium produced by the three  $\alpha$  products will be three times that produced by the radium itself.

At the beginning of each period of accumulation, however, all emanation had been removed from the radium salt. The amount of helium produced during a subsequent period of  $T$  days would therefore be equal to

$$Tx + y \int_0^T (1 - e^{-\lambda t}) dt = Tx + \left(T - \frac{e^{-\lambda T}}{\lambda}\right)y = Tx + \left(T - \frac{1}{\lambda}\right)y,$$

where  $\lambda$  is the constant of change of the radium emanation, the unit of time being taken as the day; for a value of  $T$  greater than 40 days,  $e^{-\lambda T}$  is very nearly 1.

If  $Q$  is the total quantity of helium produced in the time  $T$ , and the value  $3x$  is substituted for  $y$  in the above expression, we obtain

$$Q = \left[T + 3\left(T - \frac{1}{\lambda}\right)\right]x.$$

Substituting in this equation the values of  $Q$  and  $T$  from the two determinations, it follows that for

First determination  $x = 0.0209$  cub. mm. ;

Second determination  $x = 0.0203$  cub. mm.,

or an average production of 0.0206 cubic millimetres of helium per day by the radium (element) present in the salt used for these experiments.

The quantity of radium contained in the salt was 192 milligrams (average of 191 and 193). The production of helium per gram of radium was therefore

$$\frac{0.206}{.192} = 0.107 \text{ cub. mm. per day,}$$

and per gram of radium in equilibrium with its first disintegration products (the emanation, radium A, and radium C)

$$0.107 \times 4 \times 365 = \underline{156 \text{ cub. mm. helium per year.}}$$

The observed rate of production of helium is in very close agreement with the calculated rate of production (158 cub. mm. per year) referred to earlier, and confirms in a striking way the conclusions on which the calculations were based. There can be no doubt that the  $\alpha$  particle during its flight consists of a helium atom carrying two unit positive charges, and that helium itself is monatomic. The agreement between calculation and theory verifies in a remarkable way the essential correctness of the atomic theory of matter. The number of helium atoms expelled per second by one gram of radium have been directly counted, and the corresponding volume of helium produced has been experimentally measured. From these two experimental observations, it is possible to deduce with a minimum of assumption the number of atoms of helium in one cubic centimetre of that gas at standard pressure and temperature. This number is  $2.69 \times 10^{19}$ . By Avogadro's hypothesis this gives the number of molecules in a cubic centimetre of any gas under standard conditions.

It will be seen that this method does not involve the determination of the fundamental unit charge  $e$ , but that the value of this can be directly deduced. It is important to note that the agreement of the observed and calculated rates of the production of helium is independent of the correctness of the radium standard employed, for the same standard has been employed in both experiments. When an international radium standard is instituted, it will not be difficult to correct the rate of production of helium in terms of the new standard.

By the courtesy of Sir James Dewar we were enabled to compare the amount of radium employed in his experiments with our working standard. It was found that the quantity of radium used by Sir James Dewar, which was taken as 70 milligrams of pure radium chloride, was on our standard equivalent to 72 milligrams of  $\text{RaCl}_2$ . Expressed in terms of our standard, the rate of production of helium observed by Dewar comes out to be 164 instead of 169 millimetres per year. This is somewhat higher than our value, but is in substantial agreement with it.

*The Production of Helium by Radium Emanation.*

A determination was also made of the amount of helium produced by the disintegration of a known quantity of radium emanation. The radium emanation was obtained from a solution of radium salt, and was purified and separated from other gases by condensation at the temperature of liquid air. A soft glass tube was prepared, about 10 millimetres inside diameter and about 8 centimetres in length. At one end of this tube was a ground joint with a capillary termination similar to that on the tube *a* (fig. 1). This ground joint fitted into another tube similar to *b* (fig. 1). The glass tube was filled about half full of melted sulphur, was completely pumped out and the sulphur allowed to cool. The purified radium emanation was introduced into this tube and the tube was sealed by fusion of the glass. The tube was warmed until the sulphur melted. It was then allowed to cool and was tipped and turned in the meantime so that a continuous layer of solid sulphur about three millimetres thick was formed over the inner surface of the glass. The object of the sulphur was to provide an inner coating in which the  $\alpha$  particles expelled by the emanation and active deposit would be embedded and from which the helium could be easily displaced when the sulphur was melted. About  $19\frac{1}{2}$  hours after the emanation had been introduced into the tube, the  $\gamma$  radiation from the tube was measured and compared with that emitted by the radium standard. The results indicated that the amount of emanation in the tube at the start was equivalent to the quantity in equilibrium with 126 milligrams of radium.

Twenty-one days after the radium emanation had been introduced, the tube was warmed until the sulphur had melted and the capillary at the end of the tube was clear. The tube was then attached by means of the ground joint to the measuring apparatus, the apparatus was completely evacuated down to the joint, the capillary tube was broken

off, and the gases were pumped out and collected. During the pumping operation the tube was heated so that the sulphur melted. The tube was allowed to cool and a small amount of pure oxygen was admitted. This was then pumped out and added to the gases already obtained. The gases were introduced into the burette B (fig. 2), were passed over the heated copper oxide, introduced into the measuring portion of the apparatus, and the volume of the helium was determined in the usual manner. The gas measured was then transferred to the spectrum tube S (fig. 2), where its spectrum was examined and found to be that of pure helium. The volume of the helium found was 0.202 cubic millimetre. The amount of radium emanation in the tube at the start was the quantity in equilibrium with 0.126 gram of radium. The production of helium at first would therefore be at the rate of  $0.126 \times 3 \times 0.107$  cub. mm. per day; the factor 3 being introduced because of the three  $\alpha$ -ray changes (emanation, radium A, and radium C). Owing to the disintegration of the emanation the production of helium will decrease, however, and the total amount formed will be proportional to  $\frac{1}{\lambda}(1 - e^{-\lambda t})$ , where  $\lambda$  is the disintegration constant and  $t$  is the time. Taking the value of  $\lambda$  corresponding to a half-value period of 3.85 days for the emanation, and taking the day as the unit of time, the above expression gives 5.42; *i. e.* the amount of helium produced in 21 days will be

$$0.126 \times 3 \times 0.107 \times 5.42 = 0.220 \text{ cub. mm.}$$

The amount of helium found (0.202 cub. mm.) is in fair agreement with the amount to be expected considering the experimental difficulties.

#### *Production of Helium by Polonium.*

A determination was also made of the production of helium by polonium. The sulphides of lead, bismuth, and antimony obtained in the purification of the radium salt (p. 589) were decomposed by digesting with strong hydrochloric acid containing a small quantity of potassium chlorate. The solution was heated until the excess of hydrochloric acid was largely removed, and was diluted with weak hydrochloric acid. This solution was poured into a strong solution of ammonium sulphide. The precipitated sulphides of lead and bismuth were removed and were again treated with hydrochloric acid and potassium chlorate. An excess of sulphuric acid was added to this solution. The mixture was concentrated by evaporation and heated until the fumes of

sulphuric acid were evolved. To the residue, after cooling, a small volume of dilute sulphuric acid was added and the insoluble lead sulphate was filtered out on a small asbestos filter. The lead sulphate was decomposed by warming with strong hydrochloric acid and potassium chlorate, sulphuric acid was added to this solution and the operations just described were repeated. The two filtrates from the lead sulphate were combined, heated to boiling, and a slight excess of ammonia was added. The small precipitate of bismuth salt was filtered from the solution, and was dissolved in dilute hydrochloric acid. The volume of this solution was accurately determined and a small definite fraction of it was removed. To the main solution 5 grams of metallic copper in the form of small clippings was added, the mixture was warmed gently and was allowed to stand for several hours with frequent stirring. Under these conditions the polonium present in the hydrochloric acid solution was completely deposited in an adherent coating on the copper. The copper was washed with water and dried.

The copper with the polonium was introduced into a glass tube similar in form but smaller than that used for the radium salt (*a*, fig. 1). The air was removed from this tube and a very small amount of pure oxygen was introduced. The tube was then sealed. One hundred and twenty-eight days later, the tube containing the polonium was attached to the measuring apparatus, and the gases contained in it were pumped out. During the pumping process the lower end of the tube and the copper which it contained were heated to bright redness, in order, if possible, to displace any helium occluded in the metal. The helium contained in the gaseous mixture was determined in the usual manner and its volume was found to be 0.009 cubic millimetre. It was readily identified by its spectrum.

The small, definite fraction of the polonium solution which had been removed before treating this solution with metallic copper (see above), was diluted to about 10 cubic centimetres with water slightly acidified with hydrochloric acid. This solution was introduced into a glass vessel the bottom of which consisted of a clean plate of metallic copper. Polonium was deposited on this plate, and the number of  $\alpha$  particles expelled was kindly determined for us by Dr. Geiger. The number of  $\alpha$  particles emitted per second was equal to  $10.7 \times 10^5$ . The fraction of the solution removed was equal to  $\frac{1}{131}$ . The total number of  $\alpha$  particles emitted per second by the entire quantity of polonium was therefore  $14.0 \times 10^7$ . The number of  $\alpha$  particles emitted per

second by one gram of radium has been found by Rutherford and Geiger to be equal to  $3.4 \times 10^{10}$ . The amount of polonium present in the preparation was therefore equal to the amount in equilibrium with 4.1 milligrams of radium.

The amount of helium produced by the polonium should be proportional to  $\frac{1}{\lambda}(1 - e^{-\lambda t})$ , where  $\lambda$  is the disintegration constant of polonium and  $t$  is the time in days. The value given by this expression is 98; *i.e.* the amount of helium produced in 128 days is 96 times the amount produced per day by the quantity of polonium present at the start. The total amount of helium formed would therefore be  $0.0041 \times 0.107 \times 96 = 0.042$  cub. mm.

The amount of helium found was therefore only about 1/4 of the amount to be expected from the theory, but the discrepancy was probably due to the fact that a very large proportion of the  $\alpha$  particles emitted by the polonium were embedded in the metallic copper. When the copper was heated only a portion of the helium formed from the  $\alpha$  particles was set free. The experiment was therefore of value only in qualitatively showing the production of helium by polonium.

#### *Production of Helium in Radium D.*

Although radium D has been found to emit no  $\alpha$  particles, when a specimen of this material is allowed to stand for some time radium E and radium F (polonium), will be formed from it, and the  $\alpha$  particles from the latter may be expected to produce helium. The lead sulphate separated from the polonium solution (p. 602), and containing the radium D (radio-lead) from the original radium solution, was sealed up in an exhausted, hard glass tube for about 110 days. The lead sulphate was then heated and the gases were pumped out of the tube. The residual gas not absorbed by cooled charcoal gave a good spectrum of helium, but its volume was not determined.

#### *Summary of Results.*

The rate of production of helium by a radium salt has been accurately measured and has been found to be equal to approximately 0.107 cubic millimetre of helium per day per gram of radium (element), which is equivalent to 156 cubic millimetres of helium per year per gram of radium in equilibrium with its first disintegration products, the emanation, radium A, and radium C.

The rate of production, 158 cubic millimetres of helium

per year, calculated by Rutherford and Geiger from the results of their experiments on the number of  $\alpha$  particles emitted by radium is in excellent agreement with the rate of production which has been found.

The amount of helium by the disintegration of a known quantity of radium emanation has also been measured and has been found to correspond with the amount to be expected from theory.

The production of helium by polonium and from a preparation containing radio-lead has also been observed.

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Manchester University.

LVI. *On the Relative Number of Ions produced by the  $\beta$  Particles from the Various Radioactive Substances.* By H. GEIGER, Ph.D., and ALOIS F. KOVARIK, Ph.D., John Harling Fellow of the Victoria University of Manchester\*.

#### *Introduction.*

IN recent years many investigations have been carried out in order to settle definitely the number of  $\alpha$ -ray products present in the different radioactive series, and to determine the number of  $\alpha$  particles emitted in each transformation. The results indicate that probably in all transformations connected with the emission of  $\alpha$  rays, an  $\alpha$  particle of characteristic velocity is expelled from the disintegrating atom. In addition a comparison of the  $\alpha$ -ray activities of successive products has led to a definite knowledge of the number of these products. There is little chance that a direct  $\alpha$ -ray product has remained undiscovered in the radioactive series known at the present time.

Our knowledge of those transformations which take place with the emission of  $\beta$  rays is by far less definite. It has been suggested that in such transformations  $\beta$  particles of characteristic velocity are emitted, but recent experiments have made this conclusion very doubtful. It appears more probable at present that the  $\beta$  particles emitted from the same substance—in some cases at least—vary appreciably in speed.

At present seven transformations are known which take place with the emission of  $\beta$  particles of high penetrating power. In about as many cases the disintegration appears to be connected with the emission of soft  $\beta$  rays whose

\* Communicated by Prof. E. Rutherford



velocity exceeds only slightly the velocity of hard cathode rays.

As to the actual number of  $\beta$  particles expelled from each disintegrating atom very little is known. Direct determination of the charge, which would give such information, has so far been made only in the case of the active deposit of radium, and, at the present time, it appears to be a matter of considerable difficulty to carry out similar experiments with other radioactive materials on account of the fact that most of them are obtainable only in small quantities.

In the present paper we hope to throw some light on these problems from other considerations. If we assume for the present that the ionization produced by a  $\beta$  particle does not depend appreciably on its velocity, we can determine the relative number of  $\beta$  particles emitted from the various substances by measuring the ionization produced by them. Consider a  $\beta$ -ray product in radioactive equilibrium with an  $\alpha$ -ray product. In this case the number of  $\alpha$  particles emitted is identical with the number of atoms breaking up of the  $\beta$ -ray substance. By measuring the ionization due to the  $\beta$  rays and dividing it by the number of  $\alpha$  particles emitted per second from the substance in equilibrium, we obtain the ionization due to the  $\beta$  particles emitted from one disintegrating atom. These ratios were determined for all substances for which it was possible to carry out such measurements.

### *Experimental Details.*

The experimental method of attacking the problem, as indicated above, divides itself naturally into two parts, namely: the determination of the number of  $\alpha$  particles emitted per second and the measurement of the ionization current produced by the  $\beta$  particles.

The determination of the number of  $\alpha$  particles can be carried out by the scintillation method or by an electrical method; the latter method, being found more convenient, was generally used. In this method the active plate was placed in the centre of a silvered spherical glass bulb, 15.9 cm. internal diameter, which was exhausted in all the experiments to a pressure of 5.46 cm. of mercury, thus allowing only .571 cm. of the range of the  $\alpha$  particles to be effective in producing ionization. At this reduced pressure saturation is easily obtained, and the current measured gives readily the number of ions produced for the effective part of the range of the  $\alpha$  particle. Using the data \* given by one of us for the ionization

\* H. Geiger, Proc. Roy. Soc. A. lxxxii. p. 486 (1909).

produced by  $\alpha$  particles of different ranges, the number of  $\alpha$  particles emitted per second from the plate was calculated. The numbers thus obtained were checked in several experiments by counting the scintillations produced on a zinc sulphide screen, and a good agreement was obtained.

An accurate determination of the  $\beta$ -ray ionization is beset with numerous difficulties. It is obviously necessary to cover the active material to absorb the  $\alpha$  radiation. Since in the thin layer of aluminium used for this purpose an appreciable number of  $\beta$  particles is stopped, an extrapolation must necessarily be made to obtain the correct value for no absorption. This correction was made by determining in each case the absorption curve of the  $\beta$  rays in aluminium. The method adopted for obtaining the absorption curve was similar to that described previously by one of us\*. This has the advantage of avoiding corrections for the reflexion of the  $\beta$  particles by the absorbing foils. In addition the air inside the electroscope also absorbs some  $\beta$  particles. This was taken into account by further extrapolation for one-half of the mean path of the  $\beta$  particles in the electroscope.

The electroscope used was a copper hemisphere 20 cm. in diameter. The active material was placed in the centre so that the average path was equal to the radius. Since the  $\beta$  particles are diffusively reflected from the interior surface of the electroscope, it was necessary to make a correction for this reflexion. This was done by constructing a similar electroscope of the same size made of thin silvered paper in which the reflexion was very small. The amount of this correction was determined by finding the increased reflexions due to increased thicknesses of such paper. The correction varied somewhat for the different types of harder  $\beta$  radiations; but owing to the difficulty of obtaining an accurate value for  $\beta$  rays of different velocities, the mean of all the values obtained by using different types of rays was employed in all cases. This correction was 27 per cent. of the ionization produced in the metal hemisphere.

In order to check the accuracy of the numerous corrections which were necessary, similar experiments were made with electroscopes of widely different dimensions. In addition to the hemisphere two electroscopes cubical in shape whose lengths of edge were 12.7 and 3.84 cm. respectively were used. The active material was placed on the top of the electroscopes. The average path of the  $\beta$  particles in each

\* A. F. Kovarik, *Phil. Mag.* xx. p. 849 (1910).

was calculated graphically, and the values thus found are 10.4 cm. and 2.94 cm. respectively.

In all cases the electroscopes were standardized in absolute measure, and in addition after each experiment the sensitiveness of the electroscope in use was tested by means of a constant preparation of RaD + E which served as a standard. As will be seen from the table, the results obtained with the different electroscopes are in a reasonable agreement. For each active substance three to five experiments were carried out on each electroscope.

### *Radioactive Substances used.*

A few details regarding the radioactive substances used in these experiments may be given.

*Thorium D.*—The active material was thorium active deposit on thin aluminium-foil. Account was taken of the fact that two  $\alpha$  particles are present in the active deposit. The extrapolation for the initial value of the  $\beta$  radiation was made by using the exponential law, taking into consideration, of course, the soft rays of Th A. The absorption of Th D follows an exponential law from the smallest thicknesses of aluminium that could be used up to the thickness which cut down the activity to less than 10 per cent. of the initial value. This was tested by using pure Th D obtained by recoil.

*Actinium C.*—The active material was actinium active deposit in thin aluminium-foil. The extrapolation for the initial value of the  $\beta$  radiation was made by using the exponential law. The absorption of the  $\beta$  rays in this case was also found to obey the exponential law from the smallest thicknesses of aluminium up to those cutting down the radiation to less than 10 per cent. Pure actinium C obtained by recoil was used to test this. It may perhaps be well to note that Act B ( $\alpha$  rays) and Act C ( $\beta$  rays) require considerably different decay factors in the reduction to zero time. In two cases radioactinium preparations were used, and the rise of the  $\beta$ -ray activity was observed for several weeks. Correcting for the soft  $\beta$  radiation of radioactinium and Act X the value of the hard or Act C radiation was obtained at the time of equilibrium. The number of atoms breaking up was calculated from the determination made of the  $\alpha$ -ray activity directly after the preparation of the radioactinium plate. Experiments showed that there was no Act X present at the time. Both methods gave the same results\*.

\* This proves that radioactinium emits the same number of  $\alpha$  particles as Act B, a point which has recently been questioned.

*Radium B.*—A wire was exposed to radium emanation in an electric field for 5–10 minutes, in which time a sufficient amount of Ra A was collected. Ra B was then obtained by recoil from the Ra A, exposures being made from 5 to 25 seconds. The  $\beta$ -ray measurements were then made immediately, and were carried on for only 3 minutes. The corrections that had to be made for the growth of Ra C within that time were relatively small. The number of atoms breaking up was obtained by measuring the  $\alpha$ -ray activity of the Ra C. Both the  $\beta$ -ray and the  $\alpha$ -ray activities were reduced to the time of the maximum (33 minutes), at which time the two substances are in equilibrium. The values obtained in the different experiments did not show the same agreement as was obtained in the case of other substances.

*Radium C.*—This was obtained in two different ways, namely, by the growth from Ra B and by chemical separations from the active deposit, using Lerch's method of separation. The absorption curve of the  $\beta$  rays is complicated, as is well known, due to the fact that groups of  $\beta$  rays of different absorption coefficients are present. According to our experiments about 60 per cent. of the total activity, when corrected for absorption, is due to soft  $\beta$  rays with an absorption coefficient  $\mu$  about 50, and 40 per cent. due to hard  $\beta$  rays with an absorption coefficient  $\mu=13.5$  about. It is, however, possible that the whole of the  $\beta$  radiation of Ra C is heterogeneous\*.

*Radium E.*—Radium emanation was allowed to decay in a sealed glass tube containing a thin aluminium foil carefully protected on one side by means of paraffin. The  $\beta$ -ray activity and the  $\alpha$ -ray activity were observed over a period of nearly a year, and from the latter measurements the number of Ra E atoms breaking up was calculated. Two such specimens were used, their relative activities being in the ratio of 40 to 1. Other experiments were made using Ra E chemically separated from pitchblende residues by Prof. Boltwood.

*Uranium X.*—This is the only case in which the number of atoms breaking up was determined in a different way from that explained above. The number was calculated from the weight of uranium, knowing that 1 gram of uranium is in equilibrium with  $3.4 \times 10^{-7}$  gram of radium†, and that 1 gram of radium emits  $3.4 \times 10^{10}$   $\alpha$  particles. The actual number of UX atoms breaking up is the product of the weight of the uranium and the above two numbers.

\* See also H. W. Schmidt, *Phys. Zeits.* vii. p. 764 (1906).

† B. B. Boltwood, *Am. J. Sci.* xxv. p. 296 (1908).

Some experiments were done with films of uranium of 5.5 cm. diameter and .0088 gm. and .0036 gm. respectively of  $U_3O_8$  per sq. cm. In other experiments U X was partially separated by means of a very small quantity of iron from several grains of uranium nitrate. The exact fraction separated was determined by measuring the  $\beta$ -ray activity of the uranium nitrate solutions both before and after the separations of the U X. The nitrate was then converted into  $U_3O_8$  in order to determine accurately the number of  $\alpha$  particles. The advantage of the second method is the fact that a very thin film of comparatively very active preparation of U X was obtained. The results by the two methods were in agreement.

*Soft  $\beta$  radiations from Th A, Act A, Ra D, Radioactinium.*

—The activity of the soft  $\beta$  radiation cannot be obtained very accurately owing to the fact that the extrapolations are necessarily great, and that the values of the absorption coefficients are rather doubtful. In addition there is also another difficulty due to the presence of hard  $\beta$  rays, and the value of the soft radiations had to be obtained by the differential method. We may mention that in comparing the hard radiations with the soft radiations from preparations of actinium X and radioactinium we observe that actinium X also emits soft  $\beta$  rays.

### *Results.*

In order to illustrate the method of calculation the actual figures of one experiment are given below for a preparation of actinium C.

Ionization current in the bulb ( $P=5.46$  cm. of Hg)

$$8.69 \times 10^{-1} \text{ E.S.U.}$$

Number of  $\alpha$  particles calculated,

$$1.44 \times 10^5 \text{ per sec.}$$

$\beta$ -ray current corrected for absorption in the aluminium  
( $\mu=28.5$ ).

$$1.72 \times 10^{-1} \text{ E.S.U.}$$

Corrected for absorption by the air in the electroscope, namely, for one-half of 15 cm. air,

$$1.90 \times 10^{-1} \text{ E.S.U.}$$

Corrected for reflexion in the electroscope (27 per cent.),

$$1.39 \times 10^{-1} \text{ E.S.U.}$$

Therefore the current produced per centimetre of path at

atmospheric pressure and temperature and per atom breaking up is

$$\frac{1.39 \times 10^{-1}}{1.44 \times 10^5 \times 15} = 6.44 \times 10^{-8} \text{ E.S.U.}$$

Taking the charge of an electron as  $4.65 \times 10^{-10}$  E.S.U., this corresponds to a production of 138 ions per cm. of path in air.

1.	2.	3.	4.	5.	6.	7.	8.
Substance.	Absorption Coefficient.	Current per $\beta$ Particle.				Number of Ions produced in first cm. of path.	Whole number of Ions produced.
		Electr. I. (Hemi-sphere.)	Electr. II. (12.7 cm. <sup>3</sup> )	Electr. III. (3.84 cm. <sup>3</sup> )	Average Value.		
Actinium C ...	28.5	$6.4 \times 10^{-8}$	$6.4 \times 10^{-8}$	$6.1 \times 10^{-8}$	$6.3 \times 10^{-8}$	136	$10.0 \times 10^3$
Thorium D ...	16.3	6.3 „	6.2 „	6.3 „	6.3 „	136	17.3 „
Radium B .....	75.0	6.3 „	6.1 „	6.1 „	6.2 „	133	3.7 „
Radium C .....	13.5 to 50	4.8 „	5.0 „	5.1 „	5.0 „	108	7.7 „
Radium E .....	43.3	3.1 „	3.3 „	3.2 „	3.2 „	69	3.3 „
Uranium .....	14.4	3.5 „	3.6 „	.....	3.6 „	78	11.3 „
Thorium A ...	130	...	$20 \times 10^{-8}$				
Radioactinium.	175	...	0.7 „				
Actinium A ...	125	...	0.4 „				
Radium D .....	120	...	0.5 „				

The results obtained for the different substances are collected in the table above. Columns 3, 4, and 5 give the values of the currents due to the  $\beta$  rays for the first centimetre of path and per atom breaking up, column 6 the mean value, weight being given according to the number of experiments performed with each electroscope. From these values the number of ions produced by a  $\beta$  particle per cm. are deduced and entered in column 7. From this figure the whole number of ions produced by a  $\beta$  particle over its entire path can be found by integrating over the absorption curve. The figures thus obtained are entered in column 8.

We shall first discuss the figures given in the upper part

of the table, which are the figures referring to the more penetrating radiation. It will be noticed that the figures (column 7) for Act C, Th D, and Ra B are nearly the same, and those for Ra E and Ur X are again similar, but different from the above; for Ra C the figure is unique.

Several suggestions may be offered to account for the variations, and we intend to discuss the following possible explanations:—

(1) The differences might be attributed to a variation of the ionizing power of the  $\beta$  particles of different speed.

(2) The differences might be ascribed to an erroneous calculation of the number of atoms breaking due to the presence of unknown  $\alpha$ -ray products.

(3) The high values might be due to the presence of  $\beta$ -ray products not yet known, or to the simultaneous emission of two  $\beta$  particles from the disintegrating atom.

As to the first point, a comparison of the absorption coefficients with the figures given for the ionization (column 7) shows that this supposition cannot account for the differences; Act C and Th D both having fairly hard radiations and Ra B with a much softer radiation give about the same value. On the other hand, Ur X emitting a radiation similar to Th D, and Ra E which is much softer, give a value approximately half that of the first-named substances. This indicates that a change in ionization with velocity cannot explain the differences.

The second point raised above might at first appear plausible on account of the fact that the values for Ur X and Ra E come out about half of the values of Th D, Act C, and Ra B. If radium itself and polonium give off two  $\alpha$  particles instead of one, as assumed, the figures for Ur X and Ra E would be double, and come into some agreement with the other products. However, investigations by other observers give no indication whatever in favour of this hypothesis.

It appears to be more likely that the third suggestion is the correct explanation, although we are well aware of certain difficulties which arise. It appears necessary to assume that Act C, Th D, and Ra B, and perhaps also Ra C, emit two  $\beta$  particles, or consist of two successive products each emitting  $\beta$  rays. The recent experiments of v. Baeyer, Hahn, and Meitner\* on the deflexion of the  $\beta$  rays from the active deposit of thorium can perhaps be brought forward in support of our view, and perhaps also the measurements of Makower†, on the charge carried by the  $\beta$  rays from the active deposit of

\* v. Baeyer, Hahn, and Meitner, *Phys Zeits.* xii. p. 273 (1911).

† W. Makower, *Phil. Mag.* xvii. p. 171 (1909).

radium. In the experiments of Makower the value obtained for the charge was considerably greater than would be expected if Ra C emits only one  $\beta$  particle.

The average value of the number of ions produced by a  $\beta$  particle of high speed per centimetre of path at atmospheric pressure is 67. This value is considerably smaller than that given by Durack \* which is 127. In Durack's experiments, however, reflexion of the  $\beta$  rays was not taken into account; this reflexion increases the ionization current and decreases the charge which is received by the plate, and gives a measure of the number of  $\beta$  particles. Both these factors, if taken into account, would decrease the number of ions produced by one  $\beta$  particle.

Concerning the soft radiations, we have already pointed out the difficulties of obtaining reliable values for the number of ions produced. There can, however, be no doubt, as is shown in the table, that with the exception of thorium A, the number is very much smaller than for the penetrating radiations. This may, of course, be due to a rapid decrease of the ionizing power of the  $\beta$  rays with decreasing velocity, or it might be possible that the soft radiations are due to products which are not in direct line of transformation. Such a possibility is suggested by the recent experiments of Fajans †, which brought out the existence of a side product in the radium series. So far as thorium A is concerned, our value for the ionization compared with that of thorium D is higher than that of Hahn and Meitner ‡; but this is accounted for by the experimental arrangement. The recent experiments of v. Baeyer, Hahn, and Meitner § indicate a complexity of the rays from thorium A, as shown by photographs.

#### SUMMARY.

The relative number of ions produced by the  $\beta$  particles from the different radioactive products was determined. In each case the number of atoms of the  $\beta$  ray-substance breaking up was found from the number of  $\alpha$  particles emitted by an  $\alpha$ -rays product in radioactive equilibrium with the  $\beta$ -ray substance.

The results could best be explained by assuming that Act C, Th C, Ra B, and perhaps also Ra C emit two  $\beta$  particles, or consist of two successive  $\beta$ -ray products emitting similar

\* J. J. E. Durack, *Phil. Mag.* v. p. 550 (1903).

† K. Fajans, *Phys. Zeits.* xii. p. 369 (1911).

‡ O. Hahn and L. Meitner, *Phys. Zeits.* ix. p. 321 (1908).

§ *Loc. cit.*



types of rays. On the basis of this assumption the whole number of ions produced by a  $\beta$  particle of high speed per cm. of its path at atmospheric pressure is 67.

Our thanks are due to Professor Rutherford for his help and interest in these experiments.

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LVII. *The Ranges of the  $\alpha$  particles from Various Radioactive Substances and a Relation between Range and Period of Transformation.* By H. GEIGER, Ph.D., and J. M. NUTTALL, B.Sc., University of Manchester\*.

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IT is well known that the  $\alpha$  particles from different radioactive substances are characterized by their ranges, *i. e.* by the distance through which they can travel in air at atmospheric pressure. This was first pointed out by Bragg, and the ranges of a number of products have been determined by him and his co-workers. The method applied by Bragg to determine the ranges is well known. By means of a set of parallel tubes placed directly above the active plate  $\alpha$  rays with practically parallel paths were obtained. The ionization produced by these rays was measured at different distances in a shallow ionization vessel, and the distance in air at which the ionization just disappeared was taken as the range of the  $\alpha$  particles.

It was shown by Rutherford that at the same distance from the source at which the  $\alpha$  particles fail to produce ionization they also lose their power of producing scintillations. The observation of the scintillations at different distances from the source therefore presents another way of determining the ranges of the  $\alpha$  particles, and this method has frequently been made use of by Hahn and other observers. It appears, however, that the scintillations method gives somewhat smaller values for the ranges than the ionization method.

Great difficulty has been experienced in the determination of the ranges of the very inactive substances uranium and thorium. In these cases, the methods mentioned above are not applicable. Estimates of the ranges of these products were, however, made by Bragg†, but more accurate values

\* Communicated by Prof. E. Rutherford, F.R.S.

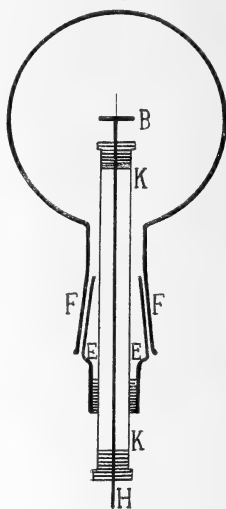
† W. H. Bragg, *Phil. Mag.* xi. p. 754 (1906).

—in the case of uranium—have recently been given by Geiger and Rutherford\*, and by Foch†.

It would be of great importance if a method could be devised which would be equally suitable for the accurate determination of the ranges of all the known  $\alpha$  ray products, but at present no such method has been found. The main difficulties result from the fact that some of the products are gases, whilst some are very feebly active or only available in the presence of other  $\alpha$  ray products.

In the present investigation we have employed a method which appears specially suitable for the determination of the ranges of the substances whose activities are small. The arrangement is indicated in fig. 1. The inside of a large glass bulb is silvered and connected to a battery of about 700 volts. The active film is placed in the centre of the bulb on a small metal disk B which is connected to the electrometer by means of the wire H. The brass tube KK surrounding the wire, and insulated from it by ebonite plugs, serves as electrostatic protection, and prevents any electrical leak from the glass bulb to the wire. The tube passes air-tight through the ground-glass joint E, which fits into the corresponding part F, sealed to the glass bulb. The length of the wire H is carefully adjusted so that the plate B is exactly in the centre of the bulb. If the pressure in the bulb is reduced the ionization produced by the  $\alpha$  particles will remain practically constant so long as the range of the  $\alpha$  particles at the particular pressure does not exceed the radius of the bulb, viz. 7.95 cm. But as soon as the pressure is decreased below that value the ionization current will also decrease. From this critical pressure and the radius of the bulb the range of the  $\alpha$  particles can easily be deduced. It adds greatly to the accuracy of the determination of the critical pressure if the active layer is very thin, and if the area over which it is spread is small. Experiments with polonium showed that plates with diameters up to 2.6 cm. could be used without introducing an appreciable error.

Fig. 1.

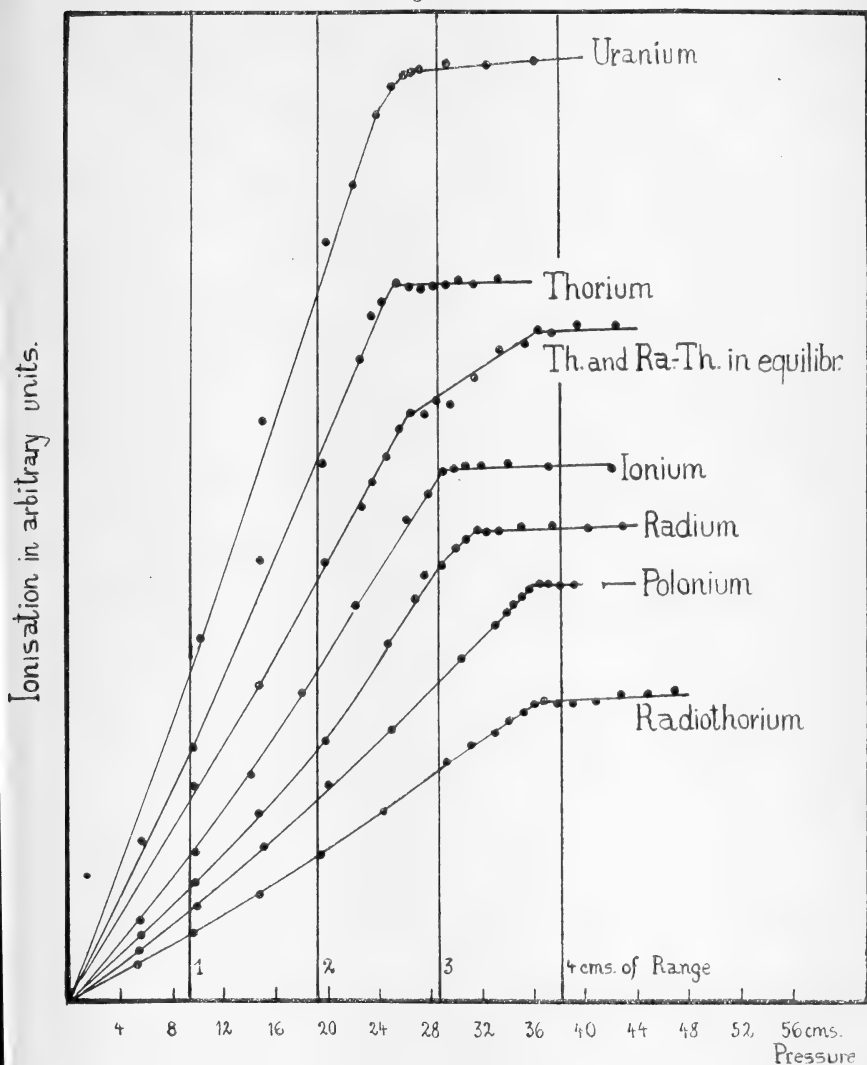


\* H. Geiger and E. Rutherford, *Le Radium*, vii. p. 225 (1910), and *Phil. Mag.* xx. p. 691 (1910).

† A. Foch, *Le Radium*, viii. p. 101 (1911).

In fig. 2 the curves for air obtained with different substances are given. The abscissæ give the pressure in

Fig. 2.



centimetres of mercury, and for convenience also the corresponding ranges reduced to 76 cm. pressure and 15° centigrade are marked. The ordinates give the ionization current measured by the electrometer for each particular

pressure. It will be seen that the critical pressure is sharply defined in each case.

A few details regarding the radioactive substances used in these experiments may be given.

1. *Uranium*.—3 mgr. of uranium oxide were spread uniformly over an area of 2.5 cm. diameter. Experiments made with thicker films gave practically the same result.

2. *Thorium*.—It is well known that thorium cannot be separated from radiothorium. Through the kindness of Prof. Boltwood we have, however, obtained some thorium which, on account of frequent precipitations over a period of many years, was repeatedly freed from mesothorium, and thus the radiothorium had practically died away. Immediately before the measurements were taken the thorium was precipitated several times in order to get rid of the thorium X and the subsequent products which might have been present.

3. *Thorium and Radiothorium in equilibrium*.—Some thorium with the radiothorium in equilibrium was separated from thorite mineral, and by several precipitations freed from thorium X and the following products. The curve shows two distinct breaks corresponding to the  $\alpha$  rays from thorium and radiothorium.

4. *Ionium*.—The source consisted of a small and hardly visible spot of ionium mixed with thorium on a thin aluminium-foil. The activity due to the thorium was too small to be detected.

5. *Radium*.—A radium solution was first freed from polonium, emanation, and active deposit. A drop of the solution was evaporated on a platinum plate and the measurements taken immediately.

6. *Polonium*.—The polonium films were prepared by bringing the polonium solution in contact with a carefully cleaned copper-foil. By electrolytic action the polonium is then deposited on the copper-foil.

7. *Radiothorium*.—Radiothorium was separated from a mesothorium preparation and freed from thorium X and the following products. A thin film was prepared and measurements taken at once.

The results for the different products employed in these measurements are collected in the following table. In each case the average value of all the measurements is given and reduced to a pressure of 76 cm. and a temperature of 15° and 0° centigrade respectively. But it must be remembered that recent investigations have shown that actually only a small fraction of the  $\alpha$  particles traverses the whole range,

and that on account of scattering and possibly other causes many are stopped at a somewhat shorter distance. One of us\* has shown that the velocity of expulsion of the  $\alpha$  particles is proportional to the cube root of its maximum range. Thus, knowing the velocity of one product the velocities of the others can be deduced. Comparison is most suitably made with Ra C, for which the initial velocity has been measured by Rutherford† and was found to be  $2.06 \times 10^9$  cm./sec. The initial velocities of expulsion calculated in this way are added in the table.

Substance.	Range 15° C.	Range 0° C.	Initial Velocity of Expulsion.
Uranium .....	2.72 cm.	2.58 cm.	$1.51 \times 10^9$ cm./sec.
Ionium .....	3.00 „	2.84 „	$1.56 \times 10^9$ „
Radium .....	3.30 „	3.13 „	$1.61 \times 10^9$ „
Polonium .....	3.77 „	3.58 „	$1.68 \times 10^9$ „
Thorium .....	2.72 „	2.58 „	$1.51 \times 10^9$ „
Radiothorium ...	3.87 „	3.67 „	$1.70 \times 10^9$ „

We have already mentioned the earlier estimates of the ranges of uranium and thorium. The range of ionium has been measured by Boltwood‡, that of radium by Bragg and Kleeman§, that of polonium by Kucera and Masek||, and by Levin¶, and that of radiothorium by Hahn\*\*. Nearly all the figures given in the table above are in fair agreement with those obtained by previous observers. In some cases, however, pressure and temperature of the air are not mentioned, so that it is difficult to make a comparison of value between the present and older determinations.

In connexion with the redetermination of the ranges of the  $\alpha$  particles from a number of products, given above and in a previous paper by one of us††, we have reconsidered the possibility of a relation between the period of the active substances and the ranges of the  $\alpha$  particles emitted by them.

\* H. Geiger, Proc. Roy. Soc. A. lxxxiii. p. 505 (1910).

† E. Rutherford, Phil. Mag. xii. p. 348 (1906).

‡ B. B. Boltwood, Amer. Journ. Sc. xxv. p. 365 (1908).

§ W. H. Bragg and R. D. Kleeman, Phil. Mag. x. p. 318 (1905).

|| Kucera and Masek, Phys. Zeitschr. vii. p. 337 (1906).

¶ M. Levin, Phys. Zeitschr. vii. p. 519 (1906).

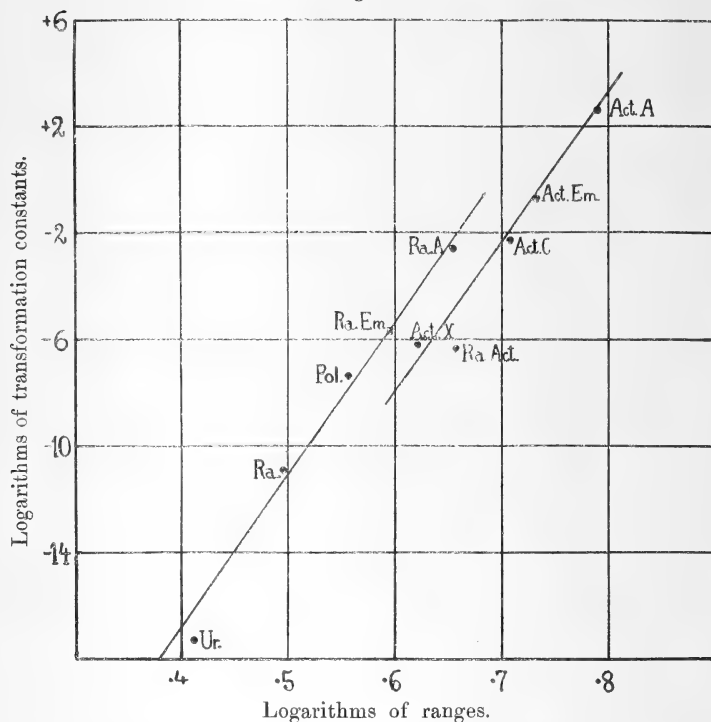
\*\* O. Hahn, Phys. Zeitschr. vii. p. 456 (1906).

†† H. Geiger, Phil. Mag. xxii. p. 201 (1911).

It has been already pointed out by Rutherford\* in 1907 that possibly a relation exists between these quantities. It appeared that the range of the  $\alpha$  particles was greater the smaller the period of transformation of the substance. There were, however, several products for which this relation did not seem to hold.

In order to find any possible relation between the range and the period we have plotted in fig. 3 the logarithms of

Fig. 3.



the transformation constants of the different products against the logarithms of the corresponding ranges for the products in the uranium-radium series and in the actinium series. The data from which these curves are plotted are given in the following table. For convenience the initial velocity of expulsion is added as well as the half-value period and the transformation constant. The ranges are reduced to 0° centigrade.

\* E. Rutherford, *Phil. Mag.* xiii. p. 110 (1907).

Substance.	Range at 0°.	Initial Velocity.	Transformation Constant.	Half-value Period.
Uranium .....	2.58 cms.	$1.51 \times 10^9 \frac{\text{cm.}}{\text{sec.}}$	$4.6 \times 10^{-18}$	$5 \times 10^9$ years
Ionium .....	2.84 "	1.56 " "	—	—
Radium .....	3.13 "	1.61 " "	$1.1 \times 10^{-11}$	2000 years
Ra Emanation ...	3.94 "	1.74 " "	$2.085 \times 10^{-6}$	3.85 days
Radium A .....	4.50 "	1.81 " "	$3.85 \times 10^{-3}$	3.0 minutes
Radium C .....	6.57 "	2.06 " "	—	—
Polonium .....	3.58 "	1.68 " "	$5.60 \times 10^{-8}$	143 days
Radioactinium ...	4.55 "	1.82 " "	$4.1 \times 10^{-7}$	19.5 days
Actinium X .....	4.17 "	1.77 " "	$7.6 \times 10^{-7}$	10.5 days
Act Emanation ...	5.40 "	1.93 " "	$1.8 \times 10^{-1}$	3.9 seconds
Actinium A .....	6.16 "	2.02 " "	350	$\frac{1}{250}$ second
Actinium C .....	5.12 "	1.90 " "	$5.4 \times 10^{-3}$	2.15 minutes

All the products in the uranium-radium series are marked on the curve except ionium and radium C. In the case of ionium the period has not yet been determined, but according to Soddy\* it is between  $5 \times 10^4$  and  $10^6$  years. It will be seen that the numbers of the uranium-radium series lie very closely on a straight line. Assuming that ionium is no exception to the rule, and taking the range of its  $\alpha$  particles to be 2.84 cm., an inspection of the curve shows that its half-value period should be nearly as high as one million years.

The discussion of radium C presents some difficulties, for from its range the half-value period of the product should be exceedingly short, about  $10^{-6}$  second. The recent work of Hahn and Meitner† and of Fajans‡ has shown that the substance ordinarily called radium C is undoubtedly complex, and that the changes occurring in these substances are perhaps irregular. There is certainly no definite evidence yet available which would contradict the possibility that the period of transformation of the product which gives rise to the long-range  $\alpha$  particles is very short.

It should be pointed out that a certain difficulty exists with regard to uranium. Boltwood§ has shown that the change in uranium gives rise to two  $\alpha$  particles for one in each of the successive products, and this has been confirmed

\* F. Soddy, *Le Radium*, vii. p. 295 (1910).

† O. Hahn and L. Meitner, *Phys. Zeitschr.* x. p. 697 (1909).

‡ K. Fajans, *Phys. Zeitschr.* xii. p. 369 (1911).

§ B. B. Boltwood, *Amer. Journ. of Sci.* xxv. p. 269 (1908).

by the scintillation method by Geiger and Rutherford\*. This may be ascribed to the existence of two successive  $\alpha$ -ray products, or to the emission of two  $\alpha$  particles in the disintegration of each atom. This latter hypothesis is excluded by the experiments of Marsden and Barratt†, who found no evidence that two  $\alpha$  particles were emitted simultaneously. In regard to the first supposition Marsden and Barratt's work also indicates that the period of the second product is more than a few seconds. It seems not impossible that there may exist two successive products, each of long period, which cannot be separated by ordinary chemical methods. For example, if the periods of these two substances were of the same order of magnitude the ranges of the  $\alpha$  particles would differ very little and therefore be difficult to distinguish.

In regard to actinium, it will be observed that the previous notation has been changed in consequence of the discovery of a new  $\alpha$ -ray product following the emanation. The new product is called actinium A, the second product actinium B, &c. The reason for the change of nomenclature is given in the following paper by Rutherford and Geiger. It will be seen from the figure that the relation between range and period is again represented by a straight line falling below the corresponding line of the uranium-radium series. Radio-actinium does not lie exactly on the line; this may be due to a slight error in the range, which is in this case difficult to determine.

The nomenclature for the active deposit of the thorium emanation has also been changed in a similar manner to that of actinium in consequence of the discovery of another quickly decaying  $\alpha$ -ray product, but the ranges of this product and of the emanation have not yet been determined with accuracy. Some preliminary experiments, however, made by one of us indicated that the numbers referring to the products of the thorium series also lie on a straight line when plotted in the same way as has been done for the uranium-radium and actinium series. The details will be discussed later when some experiments now in progress have been completed.

The connexion indicated above between the period and range is at present only empirical, but it may depend on some simple relation which may ultimately be brought to light. Similar straight lines to those above would be obtained by plotting period against initial velocity of expulsion, since the range is proportional to the third power of the velocity.

It is of interest that the relation discussed above offers a

\* H. Geiger and E. Rutherford, *Phil. Mag.* xx. p. 691 (1910).

† E. Marsden and J. Barratt, *Proc. Phys. Soc.* xxiii. p. 367 (1911).



possible explanation of the reason why no substance has been found emitting  $\alpha$  rays of range shorter than 2.58 cm. For example, the life of a substance which emitted  $\alpha$  rays of range 1 cm. would be so long, and consequently its transformation so slow, that its activity would be beyond the limits of detection by present methods.

Experiments are at present in progress with the view of determining with accuracy the ranges of the products which are yet uncertain. The result of such a complete investigation may be expected to show definitely whether the relation given holds generally for all the substances emitting  $\alpha$  rays.

We are indebted to Prof. Rutherford for his help and his interest in these experiments.

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LVIII. *Transformation and Nomenclature of the Radioactive Emanations.* By Prof. E. RUTHERFORD, F.R.S., and Dr. H. GEIGER, *University of Manchester* \*.

IN a recent paper, H. Geiger \* has described experiments which show that the emanation of actinium contains a product of very quick transformation, which emits  $\alpha$  rays of long range, 6.5 cm. in air, while the range of the  $\alpha$  particles from the emanation itself is 5.7 cm. Immediately after its formation, this new substance has a positive charge, and travels to the negative electrode in an electric field. By assuming that this positive carrier has the same mobility in air as a positive ion produced in air, it was deduced that the quick product was half transformed in about 1/500 of a second. The proof of the existence of this product at once explained the observation made some time before by Geiger and Marsden that the emanation of actinium apparently emitted two  $\alpha$  ray particles at nearly the same time. Since the new product is almost completely transformed in 1/50 of a second after its formation, the  $\alpha$  ray particle from the emanation itself would be followed within this interval by one from the new product, and the interval between them could not be detected by the eye using the scintillation method. In a previous paper, Geiger and Marsden † have also shown that the emanation of thorium emits two  $\alpha$  particles in rapid succession. In this case there was on the average a distinct interval between the appearance of two scintillations on the zinc sulphide screen, indicating

\* Communicated by the Authors.

† Phil. Mag. July 1911.

‡ *Phys. Zeit.* xi. p. 7 (1910).

that an  $\alpha$  ray product was present in the emanation which had an average life of transformation not longer than  $1/5$  of a second. These conclusions have been confirmed by further experiment. As in the case of the actinium emanation the new product has a positive charge, and in an electric field is deposited on the negative electrode. The period of transformation, however, is much longer than that for the corresponding actinium product. It is, in consequence, not practicable to determine the period of transformation by the method previously employed by Geiger for the short-lived product of the actinium emanation. In order to determine the period, weak electric fields are required, and under these conditions the loss of charge of the carriers by recombination with the ions seriously complicates the deductions from the experiments. In an accompanying paper, the times of transformation of these new products have been determined by a new and more direct method by H. Moseley and K. Fajans. It will be seen that the half-value period of transformation of the product in actinium is  $\cdot 002$  second, a value in good accord deduced indirectly by Geiger. The corresponding half-value period for the thorium product is  $\cdot 14$  second, a value within the limit indicated by the scintillation experiments of Geiger and Marsden.

The presence of these new products in the emanations of thorium and actinium can be simply illustrated by experiments in a dark room. The emanation from a strong preparation of actinium or of thorium is allowed to diffuse into a small cylindrical vessel in the centre of which is fixed a metal rod insulated from the cylinder by an ebonite cork. One terminal of a battery of about 1000 volts is connected to the rod and the other to the outside of the vessel. About one centimetre of the end of the rod is coated with a layer of zinc sulphide. In a dark room without an electric field, the zinc sulphide is seen to glow faintly due to the  $\alpha$  rays from the emanation. When the rod is connected to the negative pole of the battery, the end of the rod is seen to light brightly on the instant. This is due to the concentration of the short-lived product from the whole volume of the emanation space on to the small negatively charged rod. On disconnecting the battery the luminosity sinks instantly. By alternate application and removal of the electric field at rapid intervals, the luminosity is seen to rise and fall with it. In the case of actinium, the effect of the ordinary active deposit becomes evident after a few minutes by a slow but steady increase of the residual luminosity when the field is cut off. The effects are more strongly marked using the

emanation of thorium instead of actinium. For this purpose a tube containing an active preparation of radiothorium and mesothorium open at one end was placed at the base of the vessel. The emanation diffused from the tube into the air space. The increase of luminosity was relatively far more marked than in the case of the actinium emanation, a result probably due to the fact that a considerable fraction of the actinium product was transformed before the electric field could transport it to the negative electrode. A similar experiment was performed with a vessel containing some radium emanation; but the increase of luminosity on applying the field was small and the decrease of luminosity after the electric field was cut off was difficult to detect. In this case, the radium A of half-value period three minutes was concentrated on the rod. No appreciable effect is observed in any of the experiments if the central rod is charged positively.

In this connexion, it is of interest to recall an experiment on the actinium emanation made many years ago by Giesel \*. A narrow metal tube containing a strong actinium preparation at one end was placed with the open end downwards about 5 cm. from the surface of a zinc sulphide screen. The screen could be charged negatively to a high potential, and the cylinder connected with earth. On applying the electric field a luminous spot of light instantly appeared on the screen under the tube. Giesel suggested in explanation that a new type of radiation was emitted by the emanation which he termed the E rays. It has been generally assumed that the effect observed by Giesel was due to the concentration of the ordinary actinium deposit on the zinc sulphide screen. In the light of the experiments described in this paper, there appears to be no doubt, however, that the luminosity was initially mainly due to the very short-lived product of the actinium emanation. This travelled along the lines of force to the zinc sulphide screen and was transformed *in situ*, giving rise to the luminosity observed.

The presence of the new product in the thorium emanation and its rapid decay can be simply shown in the following way. A small brass cylinder about 6 cm. long is connected with a strong source of thorium preparation, and the ends are closed by small ebonite corks. An endless wire, which can be kept in constant movement by means of a motor, passes through small holes in the ebonite stoppers. The outside of the cylinder is connected with the positive pole of the battery, and the wire with the negative pole. Under

\* *Ber. d. D. Chem. Ges.* xxxvi. p. 342 (1903).

these conditions, the short-lived product of the thorium emanation is concentrated on the wire. The activity of the wire as it passes from the tube is examined by a zinc sulphide screen placed close to it. It is seen that the luminosity of the screen falls off as it is moved along the wire from the end of the tube. By suitably adjusting the velocity of the wire and using a long zinc sulphide screen placed close to the wire the decay of the new product is very strikingly and simply shown. A band of luminosity is seen on the screen which decreases rapidly in intensity from the point nearest the end of the tube. In order to observe a similar effect with the actinium emanation, the wire must be moved far more rapidly. By counting the scintillations at various points along the wire it is obvious that the decay of the product can be simply determined when the velocity of the moving wire is known. As, however, the method is similar in general principle with that employed by Moseley and Fajans in the paper referred to, it has not been considered necessary to give the results obtained.

It is seen that the atoms of the new products derived from the thorium and actinium emanations carry a positive charge, for they are conveyed to the negative electrode in an electric field. An interesting question arises whether the concentration of the active deposit from these two emanations on the cathode depends entirely upon the transportation of the new products to the cathode and their subsequent transformation *in situ*. For example, there is at present no certain evidence of the sign or magnitude of the charge on the residual atom which will result from the transformation of the new products when present in the gas. This is a question of considerable interest, and will be examined in detail later. The experiments of Russ \* and Kennedy † on the actinium emanation have shown that under some conditions as much active deposit appears on the anode as on the cathode, while in the case of thorium, the active deposit under normal conditions appears only on the cathode. These differences may possibly receive an explanation by taking into account the difference in the period of transformation of the short-lived products in the two cases. Some experiments are in progress to examine these points in detail.

#### *Nomenclature.*

The existence of two short-lived products following the emanations of thorium and actinium makes a change of

\* Phil. Mag. xvii. p. 412 (1909).

† Phil. Mag. xviii. p. 744 (1909).

nomenclature desirable, in order to give a definite name to each of these products, and to specify its position in the radioactive series. There seems to be no doubt that these short-lived products do not exist in the gaseous state, but behave as solids. This is borne out by the experimental results included in this paper, for there is no evidence that the products considered escape from the negatively charged wire except by the well-known process of radioactive recoil.

It seems fairly certain that the new products ought to be included as members of the "active deposits" derived from the thorium and actinium emanations. They resemble the first member of the active deposit of radium, namely radium A, in carrying a positive charge, and in their concentration on the cathode in a strong electric field. If they are considered to be members of the group of products now generally included under the term "active deposit," there is seen to be a remarkably close analogy in the successive transformations of the three emanations. It is seen that the new products are very analogous, both as regards physical properties and nature of radiation emitted, to the first product of the radium emanation, namely radium A. It is, therefore, suggested that the new product in thorium should be called thorium A, and in actinium, actinium A. In consequence it is necessary to denote the products previously called thorium A and actinium A, thorium B and actinium B respectively, and similarly for the later products.

The scheme of nomenclature proposed, starting from the emanations, is shown in the following table (p. 626), where the nature of the radiation emitted and the half-value period of transformation are added.

In this scheme, it is seen that not only are the A products similar in general character, but also the B products, for each of the latter emits easily absorbed  $\beta$  rays.

There is an apparent divergence in the mode of transformation of the third product of the three series. In the radium series, the product ordinarily called radium C emits not only  $\alpha$  rays but also  $\beta$  and  $\gamma$  rays. The third product of the actinium series, now named actinium C, emits only one type of  $\alpha$  rays, and is followed by another product to be called actinium D, emitting  $\beta$  and  $\gamma$  rays. This latter product was isolated by Hahn using the recoil method. In the case of thorium, the transformation of the second product, thorium B, is followed by a product of half-value period 55 minutes, which Hahn showed emitted two distinct types of  $\alpha$  rays, whose ranges in air are 5.0 and 8.6 cm. In all other radioactive transformations, it has been observed that each product

RADIUM SERIES.			THORIUM SERIES.			ACTINIUM SERIES.		
Substance.	Period.	Radiation.	Substance.	Period.	Radiation.	Substance.	Period.	Radiation.
Radium Emanation.	3.86 days.	$\alpha$ rays [4.23 cm.]	Thorium Emanation.	53 seconds.	$\alpha$ rays.	Actinium Emanation.	3.9 seconds.	$\alpha$ rays. [5.7 cm.]
↓			↓			↓		
Radium A.	3.0 minutes.	$\alpha$ rays [4.83 cm.]	Thorium A.	.14 second.	$\alpha$ rays.	Actinium A.	.002 second.	$\alpha$ rays. [5.5 cm.]
↓			↓			↓		
Radium B.	26.7 minutes.	soft $\beta$ rays.	Thorium B.	10.6 hours.	soft $\beta$ rays.	Actinium B.	36 minutes.	soft $\beta$ rays.
↓			↓			↓		
Radium C + C <sub>2</sub>	19.6 minutes.	$\alpha$ rays [7.06 cm.]	Thorium C + C <sub>2</sub>	55 minutes.	$\alpha$ rays. [5.0 cm.]	Actinium C.	2.15 minutes.	[ $\alpha$ rays] [5.4 cm.]
↓	1.38 minutes.	$\beta$ rays.		?	$\alpha$ rays [8.6 cm.]	↓		
Radium D.		soft $\beta$ rays.	Thorium D.	3.1 minutes.	hard $\beta$ rays.	Actinium D.	4.71 minutes.	hard $\beta$ rays.

emits  $\alpha$  particles of characteristic range. It has, therefore, been generally assumed that two successive products are present, one of period of 55 minutes emitting  $\alpha$  particles of range 5.0 cm., followed by a product of probably rapid transformation emitting  $\alpha$  particles of range 8.6 cm. Although a number of attempts have been made by various observers, it has not so far been found possible to separate the two products; for they always appear together and decay together with the same period, and each product seems to emit about the same number of  $\alpha$  particles per second.

Hahn has also shown that from a plate coated with the active deposit of thorium, a product emitting  $\beta$  and  $\gamma$  rays of period three minutes can be obtained by recoil. We thus see that the analogy apparently breaks down at this point; for radium C or actinium C emits only one type of  $\alpha$  rays. In addition, in the case of actinium and thorium, the penetrating  $\beta$  and  $\gamma$  rays arise from a distinct product following the  $\alpha$  ray transformation. Recently, however, Hahn and Meitner\* drew attention to the existence of a new product in radium C. This has been confirmed and examined in detail by Fajans†, who found that the product has a period of 1.4 minutes, and emits only  $\beta$  and probably  $\gamma$  rays. The absorption of these rays is about the same as for those ascribed to ordinary radium C. This new product is obtained by recoil from pure radium C, but in exceedingly small relative quantity, about 1/20000, measured by the  $\beta$  rays. In this respect, it differs markedly from the  $\beta$  ray products obtained by recoil from the corresponding products of thorium and actinium, where the relative quantities obtained by recoil are about 10,000 times greater. Fajans has discussed the question of the position of this new  $\beta$  ray product in the radium series, and concludes that radium C breaks up in two distinct ways, and that the new product is to be regarded as a lateral branch of the main radium series.

At the Radiology Congress in Brussels, the question of nomenclature was discussed, and it was generally agreed that if a product considered simple was shown to be complex, the original name should, if possible, be retained to signify the group, and that the individual components should be distinguished by numbers. For example, there are many practical advantages in retaining the name radium C to include the two or more components that may be present. So far only two components have been definitely distinguished, and these will be called radium C<sub>1</sub> and radium C<sub>2</sub>.

\* *Phys. Zeit.* x. p. 697 (1909).

† *Phys. Zeit.* xii. p. 369 (1911).

Fajans has suggested that the name radium  $C_2$  should be given to the new product of period 1.4 minutes. No attempt has been made in the Table to differentiate between the products of the transformation of the two component substances. The main series is supposed to follow the group as a whole.

In regard to thorium, it is proposed that the matter in the active deposit, which always emits the two distinct types of  $\alpha$  rays, should be called as a whole thorium C, and that its possible components should be called thorium  $C_1$  and thorium  $C_2$ . This nomenclature has certain advantages, for in the first place on this scheme all the C products emit  $\alpha$  rays, and the D products emit  $\beta$  rays. In the second place, there is at present no definite evidence that the components of thorium C are successive products in the ordinary sense. The question of the exact type of the transformation occurring in thorium C is a difficult one. If thorium  $C_1$  and thorium  $C_2$  are successive products, it is to be expected that a considerable quantity of  $C_2$  should be obtained by recoil under suitable conditions. Hahn, however, was unable to obtain any evidence of the separation of thorium  $C_2$  by recoil, and in consequence concluded that the period of the latter must be very short. On the other hand, Geiger and Marsden failed to observe any double scintillations from thorium C or any groupings of the scintillations small intervals of time apart\*.

This evidence is difficult to reconcile with the view that the changes are successive in the ordinary sense. Additional support to this conclusion is given by the observations first made by Bronson, and afterwards confirmed by the scintillation method by Geiger and Marsden, that the thorium emanation together with its short-period product emits four  $\alpha$  particles for two from the products thorium  $C_1$  + thorium  $C_2$  in equilibrium with it. This is difficult to account for on the view of successive products, unless it be supposed that both the emanation and the new product emit two  $\alpha$  particles for one from thorium  $C_1$  and one from thorium  $C_2$ . The evidence as a whole points strongly to the conclusion that the products are not successive, but are connected in some unusual way. There are several modes of transformation possible to account for the observed facts; but it is desirable to delay the discussion of these points until more experimental data are available.

As in the case of radium C, thorium D is supposed to be

\* These experiments made some time ago by Geiger and Marsden have not so far been published. A more detailed account will be published by them in a later paper.



a successive product of the group thorium C without any assumption whether it originates from only one of the components or both. The analogy between the general modes of the three emanations is undoubtedly very close. It appears very probable that the group radium C in reality corresponds to the group thorium C + D, and actinium C + D, although the type and order of the transformations appear to be different in each case. There are, however, still many questions to be closely examined before any decisive conclusion can be reached. The analogy between the products of the emanations has been discussed in some detail partly to give reasons for the scheme of nomenclature adopted, and partly to bring out the numerous points of similarity.

University of Manchester,  
August 1911.

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### LIX. *Radio-active Products of Short Life.*

By H. G. J. MOSELEY, B.A., and K. FAJANS, Ph.D.\*

THE ordinary methods by which the properties of radio-active substances are investigated are not suited to the study of products of short life. The shortest period hitherto measured, that of actinium emanation, period 3.9 seconds, was determined by a method of steady flow.

The emanation supplied at a constant rate from an actinium preparation was conveyed with a steady stream of air through a tube. The period was deduced from observations of the concentration of the emanation at different points along the tube.

Evidence, which will be discussed later, pointed to the existence of products of yet shorter life; the steady flow method was accordingly adapted to their investigation.

By this method the periods were determined of two products, the one successive to actinium emanation, the other to thorium emanation. The periods were found to be .0020 second and 0.14 second respectively.

Throughout this paper the new nomenclature proposed by Rutherford and Geiger † will be adopted. To avoid confusion the period will be added in brackets whenever a product is mentioned of which the name has been altered. The two products just mentioned will therefore be called Actinium A (.002 sec.) and Thorium A (.14 sec.).

The steady flow method can be used to investigate any

\* Communicated by Prof. E. Rutherford, F.R.S.

† See preceding paper.

product which can be both separated from its parent and brought to an instrument for the measurement of its radiation, provided the time interval is not large compared with the period of the product.

For the separation, advantage was taken\* of the fact that the residue after the expulsion of an  $\alpha$  particle is positively charged, and will therefore, if driven by recoil into the air, be carried to a negatively charged plate. By using the face of a rotating disk as the negatively charged plate, the separated product was quickly brought to an ionization vessel for the measurement of its radiation.

The period was deduced from the loss of activity of the plate during the time taken to pass from the one to the other of two similar ionization vessels.

The rotating disk used was built for running at high speeds, and was originally used by Schuster and Hemsalech for photographing sparks. Details of the construction will be found in their paper†. It could conveniently be run at a peripheral speed of 160 metres per second.

The disk was turned by an electric motor, and no difficulty was experienced in keeping constant the speed, which was read from a speed counter attached to the hub of the disk. When working with the product thorium A (0.14 sec.) the speed was reduced by introducing a pair of intermediate wheels between motor and disk.

Preliminary experiments showed that there were no serious difficulties involved in the use of the method. It was accordingly applied to the investigation of the supposed anomalies‡ in the decay of the recoil product from the active deposit of actinium.

It was next intended to search for products of short life associated with the emanations of actinium and thorium, the existence of which had been rendered probable by the work of Geiger and Marsden on double scintillations§.

At this stage Geiger|| by a different and ingenious method proved the existence of the new actinium product, and formed an estimate of its period.

We are much indebted to Dr. Geiger for his kindness in leaving to us the further investigation of the period of this product.

The following apparatus was used for investigating the products which follow actinium and thorium emanations.

\* Hahn and Meitner, *Ber. d. D. Phys. Gesel.* vol. xi. p. 55 (1909).

† *Phil. Trans. A.* vol. cxciii. p. 189 (1899).

‡ *Blanquies, Le Radium*, vol. vi. p. 230 (1909).

§ *Phys. Zeit.* vol. xi. p. 7 (1910).

|| *Phil. Mag.* vol. xxii. p. 201 (1911).

The actinium emanation was derived from actinium purified in this laboratory by Prof. Boltwood\* from the Royal Society residues; the thorium emanation from a preparation of mesothorium. The actinium was wrapped in blotting-paper, through which the emanation readily diffused; the mesothorium was contained in a small open tube. Either was fixed inside an ebonite box,  $4 \times 3 \times 3$  cm., open at one end, the edges of which, covered with velvet, pressed against the rotating disk, thus preventing much emanation from escaping. In front of the active material and parallel to the disk was a plate of copper gauze. When the latter was charged positively, the positively charged residue of the emanation was deposited on the face of the disk. Since electroscopes were affected by the vibration caused by the disk when rotating at high speed, ionization boxes and an electrometer were used for measuring the radiation. The two ionization boxes were of similar size and shape. The bottom of each was closed with goldbeater's-skin, which, while impervious to emanation, readily allowed  $\alpha$  particles to pass through, since its stopping power was equivalent to less than 2 cm. of air. The goldbeater's-skin was coated on its inner side with aluminium leaf in metallic connexion with the rest of the box. For measuring actinium A, the ionization boxes were placed side by side, and the ebonite box containing the actinium was close to them. In the case of thorium A, the three boxes were  $120^\circ$  apart. In either case the boxes were similarly situated with regard to the axis of rotation of the disk, the bottoms of the ionization boxes facing the disk at a distance of about half a centimetre.

The shape of the bottom of an ionization box was that of a truncated sector of the disk, while a brass plate of similar shape, slightly smaller, was insulated inside the box, parallel to the bottom. This plate could be connected to the electrometer by a wire, enclosed in a air-tight metal tube, to guard against induction disturbance and the entrance of emanation. The ionization boxes were kept charged to a potential of 400 volts, and the current which passed between the box and insulated plate was measured by a compensation method, the plate and connected quadrants of the electrometer being kept during the course of a measurement at zero potential by the use of an induction balance †.

In the case of thorium A, the thorium and radium emanations—derived from the impure mesothorium—escaping from the ebonite box, caused some ionization in the electrometer;

\* Proc. Roy. Soc. A. vol. lxxxv. p. 77 (1911).

† Townsend, Phil. Mag. vol. vi. p. 603 (1903).

so that serious error due to faulty insulation would have been introduced had the insulated system not been kept at zero potential.

The current was measured by connecting the brass plate to the electrometer for exactly one minute, and noticing both the quantity of electricity used in compensation during that time, and the deflexion of the electrometer-needle due to imperfect compensation.

Measurements were taken in the following order at intervals of two minutes of:—

I. The current through the first box due to  $\alpha$  particles from emanation and active deposit on the disk.

II. The current through the first box with a field of + 800 volts between the copper gauze and the disk.

III. and IV. Similar measurements in the second box.

In a typical experiment the following currents were observed: I. 298. II. 402. III. 183. IV. 236. The differences between II. and I. and IV. and III. were evidently due to  $\alpha$  particles from actinium A which had been deposited on the disk.

The sensitiveness of the first ionization box was known to be 13 per cent. greater than that of the second.

The ratio of the activities of the actinium A on the disk when opposite the first and second boxes was therefore  $104:53 \times 1.13$ .

If, now,  $\lambda$  is the decay constant of actinium A, and  $t$  the time taken to pass from the first box to the second

$$e^{-\lambda t} = .575.$$

The angular separation of the two boxes was  $16^\circ.4$ , and the time of one revolution was .037 sec.

Hence  $t = .00169$  sec., giving  $\lambda = 329$  (sec.) $^{-1}$ , and the half-value period  $\log_e 2/\lambda = .00211$  sec.

These measurements were always repeated about five times in the same order. Separate curves were then drawn showing the variation with time of the currents I., II., III., IV., and values of the decay ratio deduced from simultaneous values of the four currents obtained by interpolation. The growth of active deposit and any steady change in the deposition of actinium A on the disk were in this way allowed for. In some sets of experiments irregular changes took place, due no doubt to small changes in position of the ebonite box, whereby both the amount of actinium emanation escaping, the amount remaining as a source of actinium A, and the amount of activity removed from the disk by the contact of the velvet edging were altered. Such experiments

were discarded, the probable error in the mean of the various decay ratios obtained from the sets of readings deciding the value of the result.

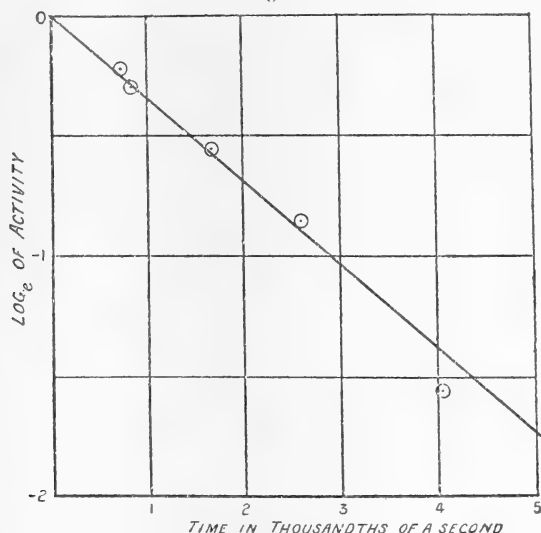
In this way the following values of  $\lambda$  were obtained

$t$ .	$\lambda t$ .	$\lambda (\text{sec})^{-1}$ .
·000726 sec.	0·234	323
·000843	0·316	375
·00169	0·562	332
·00260	0·861	332
·00405	1·56	386

Weighted mean  $\lambda = 347$ . Hence half-value period = ·00200 sec., the error being probably not greater than 5 per cent.

In fig. 1 the logarithm to base  $e$  of the activity ( $-\lambda t$ ) is plotted against the time ( $t$ ).

Fig. 1.



This result is in agreement with that of Geiger\* who, from the behaviour of actinium emanation in an electric field, deduced the existence of this new product and the order of magnitude of its period. The value given by Geiger as a rough estimate is, by a remarkable coincidence, identical with that obtained above.

It has been mentioned in the foregoing calculation that the sensitiveness of the first box was found to be 13 per cent.

\* Phil. Mag. vol. xxii. p. 201, July 1911.

greater than that of the second. This was determined by continuing the deposition of actinium A until by its decay a large quantity of active deposit had been formed on the disk. The actinium was then removed and the currents in the two boxes compared, allowance being made for the decay in activity of the deposit. The observed difference in sensitiveness may in part have been due to imperfect adjustment of the positions of the boxes, so that a little activity may have escaped the second box but not the first. It will be seen that in correcting for sensitiveness, thus determined, error due to faulty adjustment is at the same time eliminated.

In the case of thorium A, the correction for sensitiveness was made in an entirely different manner. Sets of experiments were made alternately with the disk rotating in opposite directions, the ratios of the activities then giving  $ke^{\pm\lambda t}$ , where  $k$  is the sensitiveness ratio. That value of  $k$  was then chosen which made the mean value of  $\lambda$  from all the "clockwise" experiments the same as the mean from all the "counterclockwise." In other respects the experiments on thorium A were similar to those on actinium A, but in the former case the calculation was simpler, since the growth of active deposit was usually inappreciable. Unexpected irregularities were occasionally observed, but, owing to the departure from England of one of the authors, it was not found possible to inquire into their cause. The mean value found for the half-value period of thorium A was 0.145 second, and this value is thought to be correct to within 10 per cent. A more careful determination will, however, be made as soon as work on this subject is resumed. The result is in agreement with the deduction of Geiger and Marsden\*, that an  $\alpha$ -ray product exists in thorium emanation with a period of the order of a fifth of a second.

#### *Experiments with Actinium C.*

The active deposit from actinium is known to consist of three successive products, actinium B (36 min.), C (2.1 min.), and D (4.7 min.). Mlle. Blanquies, believing the  $\alpha$  radiation of actinium C to be complex †, has suggested that it may have come from more than one product, and a product named actinium B<sub>2</sub> has obtained a provisional place in Mme. Curie's 'Radio-activity.' The results of experiments made by Mlle. Blanquies to test this question ‡ were not conclusive, but irregularities were observed in the decay of actinium C,

\* *Phys. Zeit.* vol. xi. p. 7 (1910).

† *Le Radium*, vol. vi. p. 230 (1909).

‡ *Le Radium*, vol. vii. p. 159 (1910).

and of the product obtained by recoil from the active deposit, which were consistent with the existence of a product subsequent to actinium C, with a period of a few seconds.

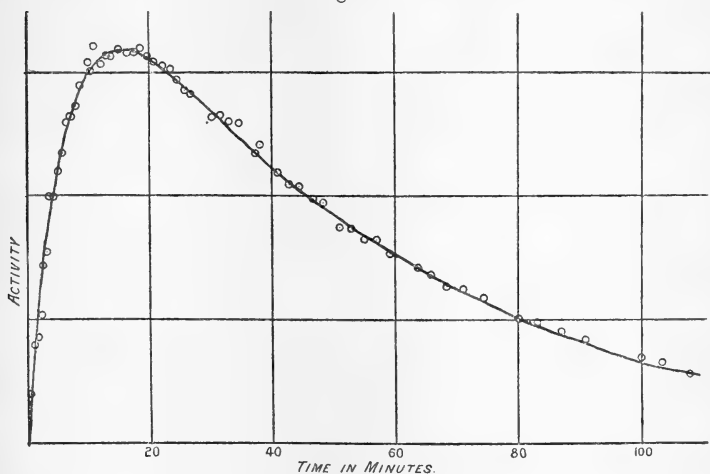
The smallness of the observed effect would be explained by the fact that no measurements were taken until a minute after the decay had started.

The existence of this product was therefore tested by the method described in this paper.

A plate rendered active by exposure to actinium emanation was placed in front of the rotating disk. Opposite the disk was an electroscope with an opening large enough to receive a fourth part of any radiation coming from the disk. The electroscope was fixed to a bracket projecting from a wall, in order to avoid the vibration set up by the rotation of the disk.

When the plate was uncharged, no activity was transferred to the disk. On charging the plate positively, those atoms which by the expulsion of an  $\alpha$  particle had been projected into the air, were carried to the disk. Such atoms consisted of actinium D and of the hypothetical new product. Since actinium D does not emit  $\alpha$  particles, the ionization in the electroscope would be mainly due to the new product, unless this product either had decayed before reaching the electroscope, or belonged to some side branch from the main disintegration series. The rise of activity on the disk, on

Fig. 2.



charging the active plate, is shown in fig. 2, the time interval before reaching the electroscope being .15 second.

The curve drawn has been calculated on the assumption that the recoil product consists entirely of actinium D, and the agreement between theory and experiment is seen to be satisfactory.

It is to be remarked that the recoil experiments of Mlle. Blanquies were complicated by the presence in the recoil product of some actinium B. We, on the contrary, always obtained by recoil, either from an active plate or from a fine wire, actinium D alone.

The presence of a product of short life would also be shown by a rapid initial fall of activity on removing the active source. The rise of activity on the disk was measured as before, until, after 15.7 minutes, the maximum was reached. The active plate was then earthed, and the activity on the disk was found to decay exponentially with the period of actinium D, the activity, immediately after the plate was earthed, being found by extrapolation to be the same as immediately before.

In the light of these experiments, the observation of Geiger and Marsden\* that 10 per cent. of the  $\alpha$  particles from actinium active deposit are emitted in pairs, seems only to be explained by the existence after actinium C of a side-branch product of very short life. Observations have been made with a small ionization vessel, and the disk rotating at high speed, in which such a product should have been detected had its period been greater than  $10^{-4}$  second.

A short description will now be given of a simple method by which products obtained by recoil may be analysed, and products of short life detected. The method is also suited to the examination of the radiation from such products.

The bottom of an electroscope is closed by a sheet of lead, in which is a large hole covered over with aluminium leaf. The active plate, the source of the recoil, is fixed, active side downwards, to the lead sheet.

Any ionization produced in the electroscope is due to  $\gamma$  radiation, and to  $\beta$  radiation reflected into the opening from surrounding objects.

Directly underneath the opening and in full view of the active plate is placed a small insulated metal plate, or reflector. This reflector being charged to a high negative potential by an influence machine, attracts to itself the product recoiling from the active plate, and the radiation from this product enters the electroscope.

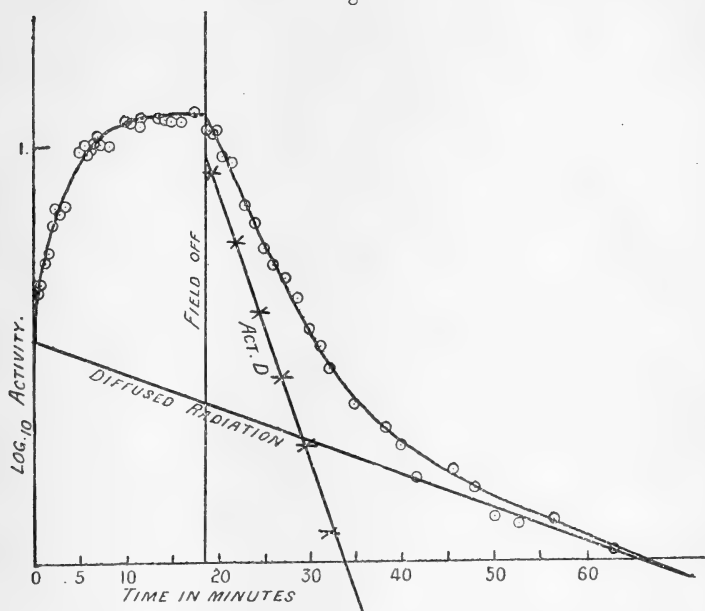
Using actinium active deposit as the source of activity the results shown in fig. 3 were obtained.

\* *Loc. cit.*



The straight line marked "Diffused Radiation" gives the effect observed when the reflector is uncharged. The upper

Fig. 3.



curve was obtained when the reflector was charged by a Wimshurst machine to a potential of about 10,000 volts, the distance between source and reflector being 5 cm. After 18 minutes the reflector was again earthed. By subtracting the diffused radiation from the latter part of the upper curve, the straight line marked "Act D" was obtained. It will be noticed that the two branches of the upper curve meet; a proof that no product of period of a few seconds has been deposited by recoil.

#### *Sensibility of the new method.*

A brief discussion will now be given of the possibilities of the new method for detection of products of very short life. The time interval between the formation of a new product and the detection of its effect depends on two factors: (1) the interval required for deposition of the active matter on the rotating disk, (2) the interval between deposition and measurement—which is determined by the angular distance of the detecting vessel from the source and the speed of rotation of the disk. The minimum time lost by a charged

atom in reaching the rotating disk is limited by the dielectric strength of the air, the velocity\* in an electric field of one volt per centimetre being about 1.4 cm. per second. The minimum time lost will therefore be about  $10^{-5}$  second.

The time lost in reaching the measuring instrument will be least when the product emits  $\alpha$  particles, and these are counted by the method of scintillations. Since the distance between source and zinc-sulphide screen need be not more than a few millimetres, measurements may be taken between  $10^{-5}$  and  $10^{-4}$  second after the separation of the product.

It is intended by this method to extend the investigation into the possible complexity of radium C and of thorium C (period 55 min.) ; preliminary experiments, in which the loss of time was much greater, having given negative results.

It is evident, however, that for a product of which the parent does not emit  $\alpha$  particles, the main difficulty will be in effecting the separation.

It is intended also to use the method for studying the nature of the  $\beta$  radiation from radium C<sub>2</sub>†, the advantage being obvious of working with a source which decays to half value with the period of radium C, 19.5 minutes, rather than with that of radium C<sub>2</sub> itself, viz. only 1.4 minutes.

By increasing the size of the ionization vessel, more than half of the activity of the separated product will be available for measurement.

#### *Summary.*

1. Actinium emanation is succeeded by a solid product, which emits  $\alpha$  particles, and has a half-value period .0020 second.

2. Thorium emanation is succeeded by a similar product with half-value period 0.14 second.

3. The product obtained by recoil from actinium active deposit is pure Act D. The supposed complex nature of Act C is therefore not confirmed.

In conclusion we wish to express our sincere gratitude to Professor Rutherford, both for the loan of much radioactive material, and for the kind interest which he has taken in this research.

Physical Laboratory,  
University of Manchester.

\* Franck, *Verhand. d. D. Phys. Gesel.* vol. xi. p. 55 (1909).

† Fajans, *Phys. Zeit.* vol. x. p. 372 (1911).

LX. *The Intensity of the Earth's Penetrating Radiation at Different Altitudes and a Secondary Radiation excited by it.*  
By Prof. J. C. McLENNAN and E. N. MACALLUM, B.A.\*

I. *Penetrating Radiation at different altitudes.*

IN a paper in the Phil. Mag. Jan. 1911, page 37, Dr. A. S. Eve, on certain assumptions, calculates the probable effect of altitude on the intensity of the  $\gamma$  rays from radium C present in the earth, and obtains the values given in Table I. below for the ionization due to this radiation at points at different heights above the ground.

In his calculations he made no correction for a decrease in the density of the air with increase in altitude, but pointed out that this would tend to augment the lower figures given in the table. He also stated in the paper that the number of ions made per cubic centimetre per second should perhaps be doubled if the effect of thorium in the earth were added to that of radium.

From the numbers given in the table it is clear that if the penetrating radiation present at the surface of the earth is entirely of terrestrial origin, it should be possible to detect a diminution in the intensity of this radiation even at moderate distances above the earth's surface.

TABLE I.

Height in Metres.	Penetrating Radiation.	
	Ratio.	Ions per cm. <sup>3</sup> per sec.
0.....	1.00	.80
1.....	.98	.78
10.....	.83	.67
100.....	.36	.29
1000.....	.001	.008

The only numbers which directly lend confirmation to Eve's conclusions appear to be given in a paper by Wulf (*Le Radium*, June 1910, and *Phys. Zeit.* 15 Sept., 1910), who found " $q$ "=6 for the number of ions made per c.c. per second by the penetrating radiation at the surface of the

\* Communicated by the Authors, having been read before the Royal Society of Canada, May 16th, 1911.

earth in Paris, and " $q$ " = 3.5 at a height of 300 metres on the Eiffel Tower.

In addition to these results some observations made by Gockel—who noted a moderate decrease in the saturation current of an electroscope which he carried in a balloon ascent of some 4 kilometres—seem to be the only ones which throw any light on the question of a diminution of the intensity of the penetrating radiation with the altitude.

In order to see if such a diminution as that indicated by Eve's numbers was observable at Toronto, a series of measurements was made at different points, both on the ground and on buildings at different heights above the ground.

The intensity of the penetrating radiation at different places was obtained by measuring with a C. T. R. Wilson electrometer \*, carrying a compensating electrical condenser, the saturation current through a mass of air confined in an hermetically sealed zinc receiver of about 30 litres capacity. The zinc of which the receiver was constructed was of the ordinary commercial variety and was not selected with any idea of being specially free from radioactive impurities. It was about 0.5 mm. in thickness.

As V. E. Pound † has shown that 7 mm. of aluminium are required to completely absorb all the different types of  $\beta$  radiation emitted by a sample of radium in equilibrium, it follows that the walls of the receiver used in these measurements were not sufficiently thick to exclude all radiations of the  $\beta$  type which might accompany, and be possibly caused by, the penetrating radiation.

From observations made at Toronto at different points in the month of March last, selected sets of consecutive readings are given in Table II.

From the table it will be seen that the value obtained for " $q$ " in a room in the physical laboratory was about the same as that obtained in the open space on the university lawn, viz., slightly over 15 ions per c.c. per second. The measurements made on the ice on Toronto Bay, however, gave a much lower value, " $q$ " = 9.3, than those made on the lawn, and confirmed the observations made by one of us and Mr. C. S. Wright ‡ in 1907 and 1908, when there was found an exceptionally low value for " $q$ " over the water of Lake Ontario.

\* Proc. of Roy. Soc. of Canada, p. 85, 1908, and Phil. Mag. Feb. 1909, p. 310.

† Proc. of Roy. Soc. of Canada, p. 53, 1908, and Phil. Mag. Jan. 1909, p. 126.

‡ Wright, Phil. Mag. Feb. 1909, p. 310.

TABLE II.

The Physical Laboratory.	The lawn, University campus.	The ice on Toronto Bay. Depth of water 5 metres. Distance from shore=400 metres.	Basement of City Hall. Engineer's room.	City Hall Clock Tower, 64 metres high.
15.2	15.1	9.3	16.5	11.9
15.3	15.2	9.2	15.9	12.2
15.5	15.0	8.9	15.2	11.6
14.9	15.2	9.0	15.7	12.7
15.1	15.1	9.8	16.3	11.8
15.5	15.2	9.0	16.6	12.4
14.6		9.8	16.9	12.2
14.9		9.4	15.7	11.8
15.2		9.8	15.5	12.1
15.8		9.1	16.4	12.4
Mean=15.2	Mean=15.1	Mean=9.3	Mean=16.1	Mean=12.1

The observations made in a room in the basement of the city hall, it will be seen, gave a mean for "*q*" of 16.1, while those made at the top of the clock tower on the building 64 metres from the ground, gave a mean of only 12.1 ions per c.c. per second.

From the evidence adduced by C. S. Wright\* it would appear that the ice and water in Toronto Bay cuts off practically all the penetrating radiation from the ground beneath. Assuming this to be so, we obtain from the numbers given in Table II. the value 5.8 for the number of ions made per c.c. per second, in the air in the receiver by the penetrating radiation present at the lawn, as well as by the secondary rays produced by this radiation at the metallic walls of the receiver, and probably, too, at the surface of the ground.

The table shows also, with the same assumption, that 2.8 represents the value for "*q*" arising from the penetrating radiation present at the top of the city hall tower and from the secondary rays excited by it. These numbers show that the effect of the penetrating radiation and its accompanying secondary radiation in ionizing the air in the receiver at the top of the tower, was only about 48 per cent. of the effect produced by similar radiations on the university lawn.

\* *Loc. cit.*

This diminution in intensity for an altitude of 64 metres is practically the same (as Table I. shows) as that calculated by Eve for a diminution in the earth's penetrating radiation.

It must be remembered, however, in this connexion that probably the walls of the tower itself were not without influence. The clock-tower was a sandstone structure with a square cross-section of about 50 square metres area, and while the building proper of the city hall was about 40 metres high, the tower extended up as a column to over 24 metres above the roof of the building. The clock-room in which the measurements were made was provided with four glass windows serving as dials for the clock, each with a diameter of about 5 metres. The room itself had an attic space above it and this again was covered with a tile roof. It is presumable that the walls of the clock-room emitted penetrating rays and also absorbed to a certain extent those coming from the outside. However, the ionization observed in the basement of the city hall was only 1 ion per c.c. per second greater than that obtained on the university lawn. Consequently the amount contributed by the tower and walls of the clock-room was probably not greater than 1 ion per c.c. per second. The absorption by the glass windows too would not be very considerable, and so one may perhaps, without sensible error, set off the one effect against the other and conclude that the readings obtained represent fairly well the relative intensities of the penetrating radiation at the surface of the earth at Toronto, and at a point 64 metres above it.

## II. *Secondary Rays produced by the Earth's Penetrating Radiation.*

In the discussion which has preceded, it has been assumed that 5.8 ions per c.c. per second represents the ionization produced in air confined in a zinc receiver by the penetrating radiation present at the surface of the earth at Toronto, and by other radiations which it may give rise to or be accompanied by.

This value is somewhat higher than that obtained by Wright\* in 1908 at Toronto, whose numbers show a difference of only 3.8 ions per c.c. per second between the readings taken on the ice of Toronto Bay, and those taken on the university lawn. It must be remembered, however, that in his experiments the lawn was covered with a layer of ice and snow to a depth of 20 centimetres, while in the present

\* Proc. Roy. Soc. A. No. 577, p. 175 (1911).

measurements the ground was bare. This difference in the condition of the ground might easily account for the difference in the results. Further support for this explanation is found in the fact that in the present investigation the readings obtained in the physical laboratory were practically the same as those obtained on the bare lawn, while in Wright's observations the readings in the laboratory were 1.7 ions per c.c. per second higher than those obtained on the lawn, when covered with ice and snow.

The conclusion that 5.8 ions per c.c. per second is approximately a measure of the normal intensity of the earth's penetrating radiation is also supported by some readings recently made (near Cape Town) by Simpson and Wright\*, who are at present attached to the Scott Antarctic Expedition. In the course of some observations made by them with an apparatus similar to that used by us, they found a difference of 6 ions per c.c. per second between the readings taken inland some 200 miles at Matjesfontain, and those taken on the 'Terra Nova' on the open sea.

A further point of interest which they noted in connexion with their observations was that the readings which they obtained on the 'Terra Nova' due to the penetrating radiation immediately on leaving land, gave a mean about 3 ions per c.c. per second higher than those they obtained some time later when the vessel was well out to sea. This increase they ascribed to the presence of radioactive matter which came from the atmosphere over the land and was deposited on the surface of the vessel when lying in port.

This effect may possibly account for a difference between some numbers recently published by Pacini† in connexion with his observations near the naval station at Livorno in Italy, and those obtained at Toronto and Cape Town. In his measurements he found a difference of only 2.4 ions per c.c. per second between the readings taken on the land near the shore and those taken on a launch on the sea some 300 metres from the shore.

The effect due to active deposits on the launch would naturally depend to some extent on the size of the latter, but on the basis of Wright's observations, one may perhaps legitimately attribute 3 ions per c.c. per second to such active deposits. This would make the ionization due to the radiation from the land at Livorno equal to 5.4 ions per c.c. per second,

\* Proc. Roy. Soc. A. No. 577, p. 175 (1911).

† *Annali dell' Ufficio Centrale Meteor. e. Geod. Italiano*, vol. xxxii. 1910, pt. 1.

and so make the readings at Toronto, Livorno, and Matjesfontain practically the same.

It would seem then that 5.8 ions per c.c. per second may be taken as representing approximately the ionization produced under normal conditions by the earth's radiation in air confined at atmospheric pressure in a zinc receiver similar to that used in the present investigation.

Since Eve has shown that 1.6 ions per c.c. per second is all that can be estimated as being produced directly by the penetrating rays coming from known radioactive substances in the soil, it follows, therefore, that about 4.2 ions per c.c. per second must be accounted for by the presence of other types of radiation.

From the observations made by a number of investigators, it is clear that one of these types is the secondary radiation produced at the walls of the zinc receiver by the penetrating rays themselves. A second type which it was thought might possibly be present and contribute to the ionization in the receiver, was a secondary radiation produced at the surface of the ground by the penetrating rays coming from the soil. Some observations were taken which seem to establish the existence of this type.

The measurements which led to this conclusion were made by taking readings on the ionization of the air in the zinc receiver as it was gradually brought up to a high and extensive brick wall forming part of a brick building which bounded the university lawn on one of its sides. These readings are recorded in Table III. and are represented by the curve in the diagram.

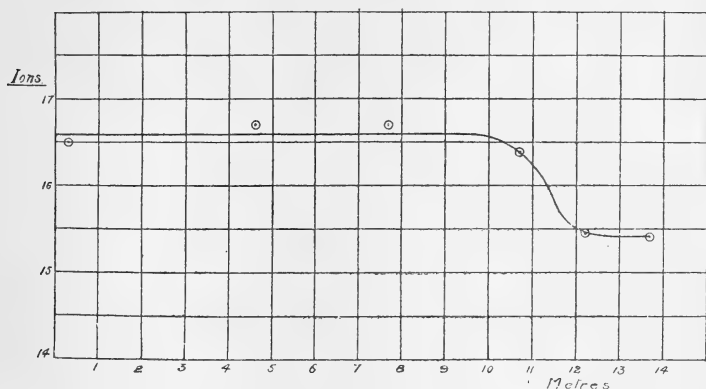
TABLE III.

Observation Station.	"q" No. of ions per c.c. per second.
At the centre of the lawn.....	15.1
13.7 metres from the wall .....	15.4
12.2   "   "   "   " .....	15.45
10.7   "   "   "   " .....	16.4
7.7   "   "   "   " .....	16.7
4.6   "   "   "   " .....	16.7
.3   "   "   "   " .....	16.5

From the numbers given in the table it will be seen that



the ionization began to increase when the receiver was about 14 or 15 metres from the wall. At the centre of the lawn the reading was 15.1, while at 13.7 metres from the wall it



was 15.4. At a distance of 10.7 metres the reading was 16.4 ions per c.c. per second, and at 7.7 metres it was 16.7. From there on to the wall the readings remained practically steady. As it had been shown previously that at any one place readings could be taken with the apparatus which did not show a variation greater than 3 per cent., it is clear from the numbers given above that the wall emitted a radiation whose range extended out in the air from the wall to a distance of between 14 and 15 metres. The absorbing power of this amount of air is roughly equivalent to between 6.5 and 7 millimetres of aluminium, and this thickness, it has been pointed out, is practically what Pound\* found necessary to cut off all the radiations of the  $\beta$  type issuing from a sample of radium in equilibrium.

It follows then that the wall emitted a radiation of the  $\beta$  type which produced a conductivity in the air in the zinc receiver corresponding to about 1.5 ions per c.c. per second.

From the nature of the observations it is impossible to determine whether this radiation was emitted directly by the wall or was a secondary radiation produced at the wall by the penetrating rays present at the surface of the earth. In either case it seems justifiable to conclude that a similar radiation was probably emitted by the soil of the lawn and contributed to the ionization obtained in the receiver when

\* Pound, *loc. cit.*

the observations were made there. It should be possible, however, to get more direct evidence of the existence of this  $\beta$  radiation from the soil by making observations at the surface of the ground in a clear space and at a point directly above in the free air about 15 metres from the ground. Such measurements should not involve great difficulty, and it is hoped shortly to undertake them. Additional observations will also be made to see if a  $\beta$  type of radiation is emitted by the walls generally of structures which are exposed to the earth's penetrating radiation.

### III. *Summary of Conclusions.*

1. At Toronto the ionization obtained in air confined in a thin-walled zinc receiver of about 30 litres capacity on the surface of the bare ground of the university lawn is greater than that obtained in the same air on the ice in Toronto Bay by about 5.8 ions per c. c. per second.

2. Evidence has been presented which goes to show that this same difference exists at Livorno, Italy, and near Cape Town in South Africa, between readings taken on the open sea and those taken on the neighbouring land.

3. As Eve\* and Simpson and Wright† have shown that the penetrating radiation over the ocean from radium and thorium in the sea is negligible, it follows that 5.8 ions per c.c. per second represents the average effect of the penetrating radiation emitted by the earth and any rays of the  $\beta$  type which may accompany it.

4. The observations at Toronto give evidence of the existence of a radiation of the  $\beta$  type accompanying the penetrating radiation from the soil which produced in the air in the zinc receiver about 1.5 ions per c.c. per second.

5. Assuming that Eve's value of 1.6 ions per c.c. per second represents the direct effect of the penetrating radiation, it follows that 2.7 ions per c.c. per second must be produced by the secondary rays emitted by the walls of the zinc receiver, or by these and by other radiations which may be emitted by the soil and which have not yet been detected.

The Physical Laboratory,  
University of Toronto,  
May 10th, 1911.

\* *Loc. cit.*

† *Loc. cit.*

LXI. *The Variation of Ionizing Power with the Velocity of Cathode Rays.* By J. L. GLASSON, B.A., B.Sc., 1851 Exhibition Scholar of Adelaide University\*.

IT is highly important that we should know the number of ions a cathode ray makes in going unit distance in a gas, and how this number varies with the velocity of the cathode ray. The only experiments which have hitherto been made on this subject are those of Durack. He† reached the conclusion that one cathode ray moving with a velocity of  $4 \times 10^9$  cm. per. sec. makes  $\cdot 4$  pairs of ions per cm. in air at a pressure of 1 mm. of mercury. Later‡ using beta rays from radium whose velocity he estimated at  $2\cdot3$  to  $2\cdot8 \times 10^{10}$  cm. per sec. he found that the number of pairs of ions made per cm. in air at 1 mm. pressure was  $\cdot 17$ . Thus increasing the velocity 6 times has decreased the number of ions produced  $2\frac{1}{2}$  times. However, in both his determinations there are several sources of error. His rays were in neither case homogeneous. In his first series he used the Lenard rays which had come through an aluminium window, and which must have been fairly completely scattered by it. The beta rays from radium which he used are known to range in velocity from  $2 \times 10^{10}$  to nearly  $3 \times 10^{10}$  cm. per second.

Moreover, in neither series did he take any adequate precautions to prevent reflexion of the rays by the electrodes used, nor did he apply any correction factor for this reflexion.

The present experiments were therefore undertaken to eliminate these sources of error.

In order to get a homogeneous bundle of cathode rays of known velocity an apparatus similar to that described by Mr. Whiddington§ was used. AB (fig. 1) represents the section of a solenoid 13 cm. long, wound in 3 layers on a brass tube of 3·70 cm. external diameter. The ends of the tube are flanged and are closed by glass plates waxed on so as to make an air-tight joint. The rays enter the solenoid by a small side tube E soldered on to the main brass tube; into E the discharge tube which is shown at D is fitted. The rays are deflected through a right angle by the magnetic field and leave the solenoid through a similar exit tube F,

\* Communicated by Sir J. J. Thomson, F.R.S.

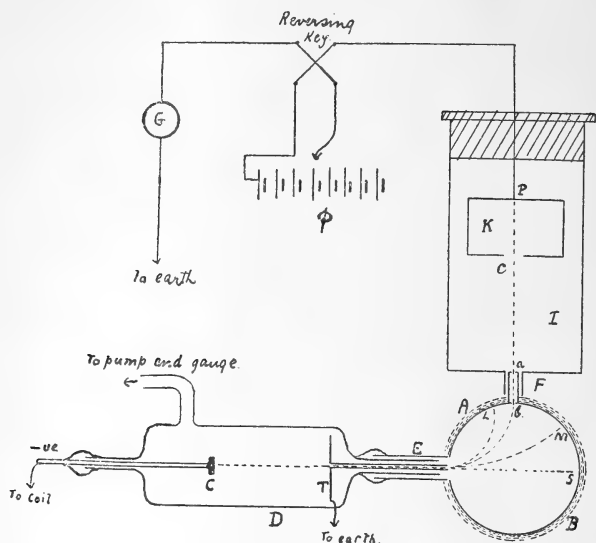
† Phil. Mag. [6] vol. iv. pp. 29.

‡ Phil. Mag. [6] vol. v. pp. 550.

§ Proc. Roy. Soc. July 1911.

and enter the ionization chamber I. Both the discharge tube and the ionization chamber are waxed on air-tight to the two side tubes of the solenoid with beeswax and resin.

Fig. 1.



The whole apparatus could be exhausted by a Töpler pump and the pressure could be measured with a McLeod gauge whose constants had been determined before setting up. As soon as the current is passed through the solenoid the rays are bent round and separated into a spectrum as at *LM*, and by suitably adjusting the current strength rays of any desired velocity may be allowed to fall on the aperture and enter the ionization chamber.

The velocity of the rays which enter the chamber corresponding to any desired current may easily be calculated when we know the dimensions of the solenoid, the current strength, and the value of  $e/m$ . The constants of the coil and the calculations are given later.

After resolution into the magnetic spectrum a small pencil of cathode rays of practically uniform velocity enters the ionization chamber through the two diaphragms *a* and *b*. The hole in each of these was about  $\frac{1}{2}$  mm. in diameter. Having traversed the chamber the rays are caught in an aluminium Faraday cylinder *K*. The outer brass case of the chamber is earthed while the Faraday cylinder can be raised to a potential sufficient to saturate the gas by a

small battery of storage-cells  $\phi$  whose other terminal is connected through a sensitive Nalder galvanometer to earth.

It is necessary that the rays should cross the chamber in a well defined beam without undergoing appreciable scattering on the way by the gas left in the apparatus. To examine how far this condition is fulfilled a willemite screen was waxed on to the end of the chamber instead of the ebonite plug and Faraday cylinder. A clearly defined spot was obtained showing no signs of scattering at any of the pressures used in the experiments. Its diameter was less than a millimetre; as the opening of the Faraday cylinder was about 4 millimetres in diameter there is no doubt that it caught all the rays.

The Faraday cylinder also does away with any effect due to reflexion of the rays. For of the rays which are reflected on hitting the top of the cylinder only those which come back normally can emerge from it. From the dimensions of the cylinder (which has been drawn to scale in the diagram), it may easily be calculated that the solid angle subtended at the point P by the aperture is less than one hundredth of the whole solid angle through which we may assume the reflected rays to be distributed. Thus the number which re-emerge is negligible.

The effective length of path of the rays in the chamber is the distance  $ac$ . There is no field inside the cylinder and any ions produced by the rays after passing  $c$ , whether before or after reflexion at P, will simply recombine and not affect the current through the chamber.

It is evident that the current through the chamber consists of two parts:—

- (1) the current carried by the rays themselves;
- (2) the ionization current.

The direction of the former is independent of the sign of the potential applied to the Faraday cylinder while the latter changes in direction when the field is reversed. By such a reversal of the potential of the Faraday cylinder we can thus obtain both the sum and difference of the effects (1) and (2).

Let  $n$  be the number of cathode rays crossing the chamber per second, and  $\alpha$  the number of pairs of ions made by one cathode ray in going 1 cm. in air at a pressure of 1 mm. of mercury, and let  $l$  be the length of path of the rays in the chamber.

Then the current carried by the rays  $= ne$ .

The saturation current carried by the ions  $= n\alpha lpe$ .

Thus when the Faraday cylinder is positively charged the current is given by

$$C_1 = ne + nalpe,$$

and when the cylinder is negative,

$$C_2 = ne - nalpe.$$

Thus,

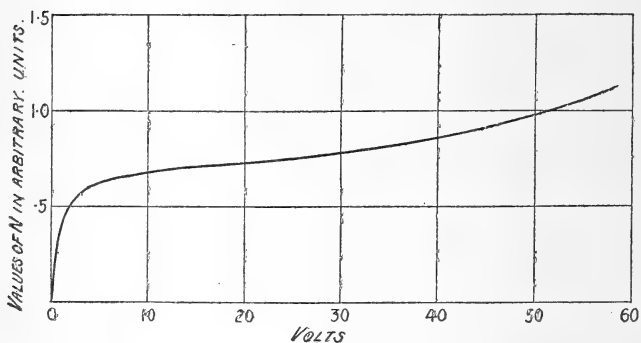
$$\frac{C_1 - C_2}{C_1 + C_2} = alp (=N).$$

It will be convenient to denote this ratio by  $N$ ; it is evidently the number of pairs of ions made by a ray in crossing the chamber.

From the ratio  $N$  knowing  $l$  and  $p$  we can at once determine  $\alpha$  or the specific ionization produced by a cathode ray.

At pressures such as those used here ionization by collision comes in for comparatively low field strengths and there is some difficulty in determining the correct voltage to apply to the gas in order to obtain saturation. One of the curves connecting  $\frac{C_1 - C_2}{C_1 + C_2} (=N)$  with voltage is shown in fig. 2.

Fig. 2.



It will be seen that ionization by collision comes in almost as soon as saturation is obtained. In these experiments a potential of 6 volts was applied to the cylinder.

### Results.

The method of taking the readings is as follows. The apparatus was exhausted down to a pressure at which the cathode rays begin to be produced. The current through

the solenoid was adjusted by resistances to a definite value indicated by a Weston ammeter and the values of  $C_1$  and  $C_2$  observed on the galvanometer scale. The solenoid current was then altered so as to cause a different part of the spectrum to enter the chamber and the galvanometer deflexions again read. Readings were taken in this way throughout the range of the spectrum. The pressure was then altered and a fresh set of readings taken over the range of velocities obtained.

In practice, the range of velocities which can be used is limited both at its lower and upper ends. The velocity of the rays produced by the discharge depends on the pressure in the tube. The highest pressure at which cathode rays appear at  $s$  was found to be .21 mm. of Hg. It was found that the slowest rays produced at this pressure had a velocity corresponding to 6 amperes, *i.e.* it required a current of 6 amperes in the solenoid to deflect them into the ionization chamber. The upper limit to the velocities employable is governed by the following considerations. To produce fast rays the pressure in the apparatus must be reduced and consequently the number of ions produced by a ray in crossing the chamber is also reduced. Now theoretically the most accurate values of  $\frac{C_1 - C_2}{C_1 + C_2} (=N)$  are obtained when

the difference between  $C_1$  and  $C_2$  is as great as possible. For small errors in reading both  $C_1$  and  $C_2$  produce a much greater proportionate error in their difference. So that when  $C_1 - C_2$  is small the liability to error in the value of  $N$  is very great. Although a few readings were taken with a low pressure and velocities corresponding to 10 or 11 amperes they were discarded for the above reasons and no readings are given for velocities greater than 9 amperes.

The results of the experiments in air are shown in Table I. Column I. gives the pressure in the apparatus in readings of the McLeod gauge; column II. gives the current flowing through the solenoid in amperes; column III. the mean

values of the ratio  $\frac{C_1 - C_2}{C_1 + C_2}$ , *i.e.* the actual number of ions made by a ray in traversing the chamber.

In fig. 3 (p. 653) the values of  $N$  have been plotted against the pressure in the tube for different velocities of rays. It is evident that the number of ions made should be proportional to the pressure in the tube and the curves connecting the two should be straight lines passing through the origin of coordinates. The curves in fig. 3 have been obtained by

joining the origin to the centroids of each set of points. It will be seen that the points fit the curves fairly well.

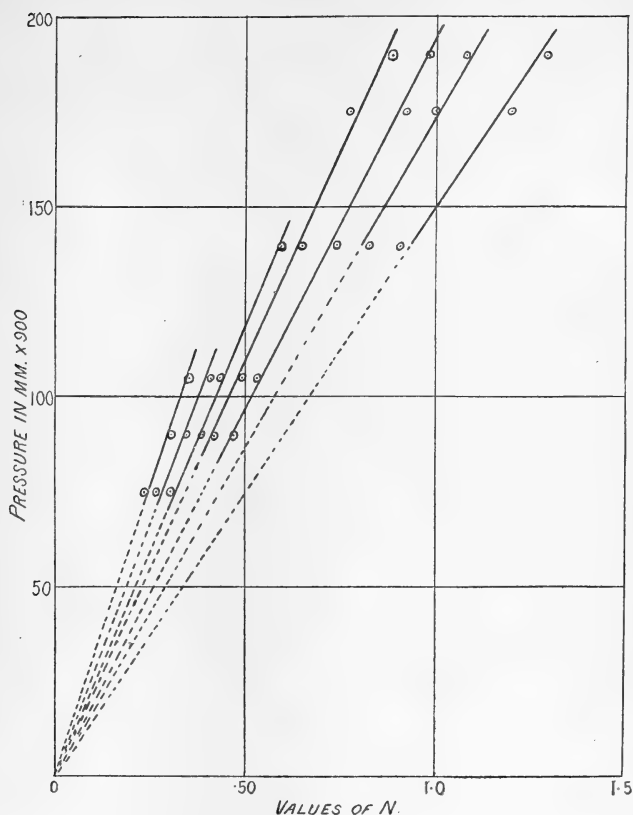
TABLE I.

I. Pressure in mm. $\times 900$ .	II. Current in solenoid (amps.)	III. $\frac{C_1 - C_2}{C_1 + C_2} = N$ .	IV. $\frac{N}{P \times 900}$
190	6	1.26	.0066
	6.5	1.09	.57
	7	.97	.51
	7.5	.86	.45
175	6	1.17	.0067
	6.5	1.01	.58
	7	.90	.51
	7.5	.80	.46
140	6	.94	.0067
	6.5	.81	.58
	7	.72	.51
	7.5	.64	.46
	8	.58	.41
105	7	.53	.0050
	7.5	.48	.46
	8	.44	.42
	8.5	.40	.38
	9	.35	.33
90	7	.47	.0052
	7.5	.42	.47
	8	.38	.42
	8.5	.34	.38
	9	.30	.33
75	8	.32	.0043
	8.5	.28	.37
	9	.25	.33

In order to plot the variation of ionization with velocity of the cathode rays, the values of  $N$  given in Table I. column III. have been reduced to a standard pressure by dividing the numbers in column III. by those in column I. It will be seen that the numbers obtained for each of the different velocities of rays agree to within about 4 per cent. To get the most probable value the means have been taken, and these are entered in Table II., column III. (p. 654) against the corresponding velocity in column I.



Fig. 3.



The numbers in column II. give the velocity of the rays in cm.  $\div 10^9$  per sec.; those in column IV. give the absolute values of  $\alpha$  corresponding to the values of  $\frac{N}{P \times 900}$  in column III. The method of calculating these columns is given later.

In fig. 4, curve I., the figures in column IV. have been plotted against those in column II. This curve represents therefore the variation of specific ionization with the velocity of the rays.

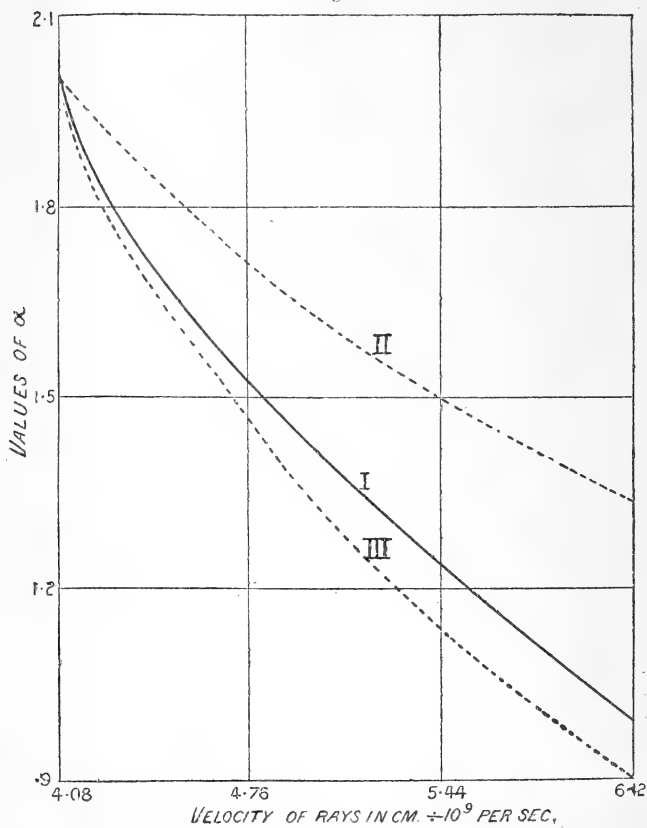
In the same figure have been plotted the curves which would have been obtained if the ionization had been inversely proportional to the first and second powers of the velocity. These are shown in curves II. and III. respectively.

It seems in this region the rate of variation is intermediate

TABLE II.

I. Velocity of rays in amperes.	II. Velocity in cm. $\times 10^{-9}$ .	III. $\frac{N}{P \times 900}$ .	IV. Values of $\alpha$ .
6	4.08	.0067	2.01
6.5	4.42	.00575	1.72
7	4.76	.0051	1.53
7.5	5.10	.0046	1.38
8	5.44	.0042	1.26
8.5	5.78	.00375	1.12
9	6.12	.0033	.99

Fig. 4.



between an inverse first-power and an inverse second-power law and is much nearer to the latter than to the former.

*Calculation of the absolute number of ions made by a Cathode Ray of known velocity.*

Hitherto the values given for the number of ions and the velocity of the rays have been purely relative. It is important to get some definite numerical estimate of the specific ionization made in air by a cathode ray of known velocity.

The dimensions of the solenoid were as follows :—

Internal diameter of windings .....	= 3.70 cm.
External diameter of windings.....	= 4.65 „
Total number of turns in the three layers	= 231
Total length of solenoid .....	= 13.0 cm.

The calculated value of the field at the centre obtained by summing the magnetic force at the centre due to each turn over the whole length of the solenoid gives a value of  $H = 20.8$  gauss per ampere. The field strength was tested experimentally with a small search-coil and a ballistic galvanometer, each of which had been previously standardized. With 5 amperes flowing through the solenoid the field strength was found to be 109 gauss at the centre and 105 gauss at the sides. This gives as a mean 107 gauss or 21.4 gauss per ampere. This differs from the calculated value by less than 3 per cent., which is satisfactory in view of the roughness of the winding and the degree of accuracy obtainable in the rest of the measurements. We may take the value of  $H$  to be 21 gauss per ampere—a mean of the calculated and experimental values.

The radius of the circle into which the rays are bent to enter the aperture is equal to the internal radius of the tube which was 1.77 cm. From the formula  $\rho = \frac{mv}{eH}$  we find the velocity of the rays is  $6.8 \times 10^8 \times C$  where  $C$  is the solenoid current in amperes.

The readings obtained for  $N$  are considered to be most accurate when the current in the solenoid was 7 amperes. For then the number of cathode rays was large and also the difference between  $C_1$  and  $C_2$  was fairly great. From column III. of Table II. the mean value of  $\frac{N}{P \times 900}$  for 7 amperes is .0051.

Now  $\alpha = \frac{N}{Pl}.$

In all these experiments the length  $l$  was 3.00 cm. So that  $\alpha = 1.53$ .

Therefore 1 cathode ray moving with a velocity of  $7 \times 6.8 \times 10^8 = 4.8 \times 10^9$  cm. per sec. makes 1.5 pairs of ions in going 1 cm. in air at a pressure of 1 mm. of Hg.

It is interesting to compare this value with that obtained by Durack. He found that 1 cathode ray moving with a velocity of  $4 \times 10^9$  cm. per sec. makes .43 pairs of ions per cm. In the light of more recent experiments, his determination of the velocity may be corrected. In applying the formula  $v = H \frac{e d^2 + \delta}{m 2\delta}$  to determine the velocity from the magnetic deflexion, he made  $\frac{e}{m} = 10^7$  instead of the more correct value  $1.8 \times 10^7$ . This would make the velocity of his rays  $7.2 \times 10^9$  cm. per sec. Assuming that the ionization varies inversely as the square of the velocity, for a velocity of  $11.8 \times 10^9$  cm. per sec. we get  $\alpha = .97$ . The value obtained in these experiments was 1.5. The agreement is as good as might be expected.

I desire to thank Sir J. J. Thomson for his inspiring interest and advice in these experiments.

Caius College,  
July 20, 1911.

## LXII. *The Mode of Conduction in Gases.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a paper on "The Mode of Conduction in Gases illustrated by the Behaviour of Electric Vacuum Tubes" that appeared in the July Number of the Philosophical Magazine, Sir Oliver Lodge has put forward a theory to explain how the conductivity is produced. A good many theories of these phenomena have been proposed which are in some points consistent and founded on experimental evidence, but there are few in which so many imaginary properties are attributed to the molecules. To mention an instance the following passage may be quoted. "In an active vacuum-tube the continual presence of such ions near the cathode depends on their having been able to travel from the anode; nevertheless they are not atoms of the anode itself, but are gas atoms which have become positively charged by contact with it,—each of them having presumably given up an electron to the metal.

"It is at the surface of the anode therefore that the separation of electricities really takes place, under stress of the applied E.M.F. The ions then migrate to the cathode, and

extract from it an electron apiece, thereby becoming neutral again.

“A constant diffusion of uncharged atoms towards the anode and of positively charged ions away from it is therefore essential to the passage of current.”

It is difficult to see how these effects at the anode are essential, as electrodeless discharges are easily produced or a discharge from a negative point in which there is but a small force at the surface of the positive electrode, and consequently no positive charge would be communicated to the atoms; but these difficulties are not the most formidable objection to this part of the theory.

It may perhaps be of interest to students who are confused with the multitude of these theories, if I mention an experimental fact that is known to and accepted by the majority of physicists. *No positively electrified particles are given off from a positively charged surface at ordinary temperatures, either molecules, atoms, or corpuscles of the gas in contact with the metal, or particles emanating from the metal, no matter how great the electric force is at the surface.* The only exceptions occur in the case of  $\alpha$  particles from radioactive substances. It is possible to have a much higher electric force at the surface of a metal than occurs in an ordinary discharge-tube, and no appreciable current can be detected by sensitive apparatus. An experiment on this subject by J. E. Almy (Philosophical Magazine, September 1908) may be mentioned. He found that a current does not pass through air at atmospheric pressure between two electrodes at a distance apart of the order of a wave-length of light when the potential difference is 300 volts. If particles of the gas were to become charged by contact with an electrified surface, the phenomena should have been observed under these conditions, as the force at the surface of the metal was of the order of  $10^6$  or  $10^7$  volts per centimetre.

JOHN S. TOWNSEND.

Electrical Laboratory, Oxford.  
26th August, 1911.

*Reply by* Sir OLIVER LODGE.

It is plain that Professor Townsend regards with favour, or, shall we say, holds quite dogmatically, the opinion that electric convection in a partial vacuum is effected entirely by negatively charged carriers. That, or some approach to it, is the natural supposition, and may possibly still turn out to be true; but recently I have not found it explanatory of the phenomena exhibited by electric vacuum-valves, and accordingly I have suggested another hypothesis for consider-

ation, on the ground that it has served as a most useful clue towards experiment and design of apparatus—stating it with brevity, as explained in my paper.

That paper was not concerned with discharge round a closed contour in a self-contained completely-gaseous circuit, which is a simpler matter: it is manifest that statements about the behaviour of electrodes are not applicable when there are no electrodes.

The possibility that inconspicuous positive ions may after all be the main carriers of current for the greater part of the distance between electrodes seems to me consistent with Sir J. J. Thomson's old measurement of the speed at which positive luminosity travels from the anode in a long tube, which can be conveniently referred to in his Clarendon Press 1893 volume, 'Recent Researches,' §§ 105, 106, 107, p. 118; Proc. Roy. Soc. vol. xlix. p. 84. See also, as to the influence of bounding surfaces or discontinuities like electrodes, § 86, p. 103 of the same book.

LXIII. *Tables of Neumann Functions  $G_n(x)$  and  $Y_n(x)$ . By JOHN R. AIREY, M.A., B.Sc., late Scholar of St. John's College, Cambridge\*.*

(A.)

THE values of the functions  $G_0(x)$  and  $G_1(x)$  have been calculated by Aldis† to 21 decimal places from  $x=0.1$  to 6.0 by intervals of 0.1. In a paper by Michell on "The Wave-resistance of a Ship," tables of these functions in the form

$$\kappa J_0(x) - Y_0(x) \text{ and } \kappa J_1(x) - Y_1(x),$$

where  $\kappa = \log 2 - \gamma = .11593 \dots$

were given by Smith‡ from  $x=0.00$  to 1.00 and from 1.0 to 10.3. The calculations were carried out to four places of decimals with an error of one in the last place and possibly of two when the value of  $x$  is greater than 3 or 4.

The following values of the  $G_0(x)$  and  $G_1(x)$  functions were calculated from the semiconvergent series

$$G_0(x) = -\sqrt{\frac{\pi}{2x}} \left\{ P_0 \sin \left( x - \frac{\pi}{4} \right) + Q_0 \cos \left( x - \frac{\pi}{4} \right) \right\}$$

$$G_1(x) = \sqrt{\frac{\pi}{2x}} \left\{ P_1 \cos \left( x - \frac{\pi}{4} \right) - Q_1 \sin \left( x - \frac{\pi}{4} \right) \right\}$$

\* Communicated by the Author.

† Aldis, Proc. Roy. Soc. lxi., 1899-1900.

‡ Michell, Phil. Mag. [5] xlv., 1898.

and the results verified from the relation

$$G_1 J_0 - G_0 J_1 = \frac{1}{x}.$$

The  $G$  functions can also be calculated from the  $J$  functions, and this provides another method of verification:—

For large values of  $x$ ,

$$J_0(x) = \sqrt{\frac{2}{\pi x}} \cdot \left\{ P_0(x) \cos\left(x - \frac{\pi}{4}\right) - Q_0(x) \sin\left(x - \frac{\pi}{4}\right) \right\}$$

and

$$G_0(x) = -\sqrt{\frac{\pi}{2x}} \left\{ P_0'(x) \sin\left(x - \frac{\pi}{4}\right) + Q_0(x) \cos\left(x - \frac{\pi}{4}\right) \right\}$$

Put  $Q_0(x) = R_0 \sin \theta_0$  and  $P_0(x) = R_0 \cos \theta_0$ .

Then

$$\tan \theta_0 = Q_0(x) / P_0(x) \text{ and } \theta_0 \text{ can be found.}$$

Hence

$$G_0(x) = -\frac{\pi}{2} \cdot J_0(x) \cdot \tan\left(x - \frac{\pi}{4} + \theta_0\right).$$

Similarly,

$$G_1(x) = +\frac{\pi}{2} \cdot J_1(x) \cdot \cot\left(x - \frac{\pi}{4} + \theta_1\right),$$

where

$$\tan \theta_1 = Q_1(x) / P_1(x).$$

The following interpolation formulæ may be used in connexion with these tables, viz. :—

$$\begin{aligned} G_0(x \pm h) &= \left\{ 1 - \frac{h^2}{2} \pm \frac{h^3}{6x} + \frac{h^4}{24} \left(1 - \frac{3}{x^2}\right) \dots \right\} \cdot G_0(x) \\ &\quad + \left\{ \mp h + \frac{h^2}{2x} \pm \frac{h^3}{6} \left(1 - \frac{2}{x^2}\right) - \frac{h^4}{12x} \left(1 - \frac{3}{x^2}\right) \dots \right\} \cdot G_1(x), \\ G_1(x \pm h) &= \left\{ 1 \mp \frac{h}{x} - \frac{h^2}{2} \left(1 - \frac{2}{x^2}\right) \pm \frac{h^3}{3x} \left(1 - \frac{3}{x^2}\right) + \frac{h^4}{24} \left(1 - \frac{6}{x^2} + \frac{15}{x^4}\right) \dots \right\} \cdot G_1(x) \\ &\quad + \left\{ \pm h - \frac{h^2}{2x} \mp \frac{h^3}{6} \left(1 - \frac{3}{x^2}\right) + \frac{h^4}{24x} \left(2 - \frac{9}{x^2}\right) \dots \right\} \cdot G_0(x). \end{aligned}$$

For comparison, it may be noted that  $G_n(x)$  is the same as

$$-\frac{\pi}{2} Y_n(x) \text{ [Nielsen]}, \quad -\frac{\pi}{2} K_n(x) \text{ [Graf u. Gubler]},$$

$$\frac{\pi}{2} Y_n(x) \text{ [Schafheitlin]}, \text{ and } -\frac{\pi}{2} N_n(x) \text{ [Jahnke u. Emde]}.$$

TABLE I.

Greatest error '0000001.

$x$ .	$G_0(x)$ .	$G_1(x)$ .	$x$ .	$G_0(x)$ .	$G_1(x)$ .
0.1	+ 2.4099764	+ 10.1456967	5.1	+ 0.5051719	- 0.1786568
0.2	+ 1.6981963	+ 5.2210521	5.2	+ 0.5203278	- 0.1243919
0.3	+ 1.2680624	+ 3.6020011	5.3	+ 0.5300453	- 0.0699752
0.4	+ 0.9519412	+ 2.7973873	5.4	+ 0.5343345	- 0.0159079
0.5	+ 0.6982484	+ 2.3113834	5.5	+ 0.5332549	+ 0.0373194
0.6	+ 0.4846062	+ 1.9798181	5.6	+ 0.5269145	+ 0.0892301
0.7	+ 0.2994958	+ 1.7329808	5.7	+ 0.5154680	+ 0.1393663
0.8	+ 0.1363487	+ 1.5364653	5.8	+ 0.4991149	+ 0.1872925
0.9	- 0.0088409	+ 1.3715040	5.9	+ 0.4780969	+ 0.2325990
1.0	- 0.1386337	+ 1.2271262	6.0	+ 0.4526952	+ 0.2749056
1.1	- 0.2547254	+ 1.0966036	6.1	+ 0.4232276	+ 0.3138641
1.2	- 0.3582727	+ 0.9756787	6.2	+ 0.3900442	+ 0.3491624
1.3	- 0.4500887	+ 0.8616128	6.3	+ 0.3535262	+ 0.3805244
1.4	- 0.5307644	+ 0.7526423	6.4	+ 0.3140784	+ 0.4077157
1.5	- 0.6007494	+ 0.6476520	6.5	+ 0.2721286	+ 0.4305415
1.6	- 0.6604050	+ 0.5459743	6.6	+ 0.2281207	+ 0.4488507
1.7	- 0.7100424	+ 0.4472469	6.7	+ 0.1825125	+ 0.4625354
1.8	- 0.7499480	+ 0.3513320	6.8	+ 0.1357687	+ 0.4715324
1.9	- 0.7804030	+ 0.2582480	6.9	+ 0.0883629	+ 0.4758218
2.0	- 0.8016962	+ 0.1681262	7.0	+ 0.0407618	+ 0.4754287
2.1	- 0.8141339	+ 0.0811766	7.1	- 0.0065688	+ 0.4704202
2.2	- 0.8180460	- 0.0023370	7.2	- 0.0531718	+ 0.4609071
2.3	- 0.8137909	- 0.0821170	7.3	- 0.0986050	+ 0.4470397
2.4	- 0.8017576	- 0.1678477	7.4	- 0.1424408	+ 0.4299079
2.5	- 0.7823671	- 0.2292077	7.5	- 0.1842752	+ 0.4070381
2.6	- 0.7560723	- 0.2958808	7.6	- 0.2237263	+ 0.3813912
2.7	- 0.7233573	- 0.3575642	7.7	- 0.2604405	+ 0.3523587
2.8	- 0.6847352	- 0.4139761	7.8	- 0.2940957	+ 0.3202622
2.9	- 0.6407463	- 0.4648616	7.9	- 0.3244022	+ 0.2854469
3.0	- 0.5919546	- 0.5099974	8.0	- 0.3511068	+ 0.2482808
3.1	- 0.5389448	- 0.5491967	8.1	- 0.3739929	+ 0.2091495
3.2	- 0.4823181	- 0.5823120	8.2	- 0.3928844	+ 0.1684534
3.3	- 0.4226887	- 0.6092380	8.3	- 0.4076450	+ 0.1266023
3.4	- 0.3606789	- 0.6299133	8.4	- 0.4181801	+ 0.0840132
3.5	- 0.2969150	- 0.6443225	8.5	- 0.4244371	+ 0.0411053
3.6	- 0.2320223	- 0.6524959	8.6	- 0.4264047	- 0.0017028
3.7	- 0.1636211	- 0.6545106	8.7	- 0.4241139	- 0.0439995
3.8	- 0.1013215	- 0.6504898	8.8	- 0.4176355	- 0.0853815
3.9	- 0.0367188	- 0.6406022	8.9	- 0.4070808	- 0.1254585
4.0	+ 0.0266105	- 0.6250602	9.0	- 0.3925994	- 0.1638571
4.1	+ 0.0881132	- 0.6041189	9.1	- 0.3743773	- 0.2002230
4.2	+ 0.1472640	- 0.5780732	9.2	- 0.3526337	- 0.2342253
4.3	+ 0.2035688	- 0.5472556	9.3	- 0.3276212	- 0.2655609
4.4	+ 0.2565683	- 0.5120335	9.4	- 0.2996198	- 0.2939520
4.5	+ 0.3058419	- 0.4728055	9.5	- 0.2689370	- 0.3191542
4.6	+ 0.3510101	- 0.4299980	9.6	- 0.2359018	- 0.3409553
4.7	+ 0.3917372	- 0.3840617	9.7	- 0.2008649	- 0.3591787
4.8	+ 0.4277338	- 0.3354674	9.8	- 0.1641908	- 0.3736818
4.9	+ 0.4587583	- 0.2847016	9.9	- 0.1262564	- 0.3843620
5.0	+ 0.4846184	- 0.2322629	10.0	- 0.0874480	- 0.3911526



TABLE I. (continued).

$x$ .	$G_0(x)$ .	$G_1(x)$ .	$x$ .	$G_0(x)$ .	$G_1(x)$ .
10.1	- 0.0481436	- 0.3940261	13.1	+ 0.0894179	+ 0.3380535
10.2	- 0.0087733	- 0.3929909	13.2	+ 0.0553523	+ 0.3427052
10.3	+ 0.0303139	- 0.3880964	13.3	+ 0.0209911	+ 0.3439302
10.4	+ 0.0687201	- 0.3794266	13.4	- 0.0132827	+ 0.3417416
10.5	+ 0.1060764	- 0.3671018	13.5	- 0.0472449	+ 0.3361863
10.6	+ 0.1420237	- 0.3512762	13.6	- 0.0804483	+ 0.3273439
10.7	+ 0.1762211	- 0.3321368	13.7	- 0.1126076	+ 0.3153250
10.8	+ 0.2083479	- 0.3099008	13.8	- 0.1434122	+ 0.3002710
10.9	+ 0.2381063	- 0.2848144	13.9	- 0.1725664	+ 0.2823520
11.0	+ 0.2652257	- 0.2571470	14.0	- 0.1997937	+ 0.2617651
11.1	+ 0.2894597	- 0.2271953	14.1	- 0.2248377	+ 0.2387317
11.2	+ 0.3105979	- 0.1952699	14.2	- 0.2474666	+ 0.2134960
11.3	+ 0.3284589	- 0.1617012	14.3	- 0.2674724	+ 0.1863226
11.4	+ 0.3428950	- 0.1268323	14.4	- 0.2846758	+ 0.1574914
11.5	+ 0.3537937	- 0.0910159	14.5	- 0.2989253	+ 0.1273006
11.6	+ 0.3610784	- 0.0546110	14.6	- 0.3101008	+ 0.0960550
11.7	+ 0.3647084	- 0.0179793	14.7	- 0.3181120	+ 0.0640708
11.8	+ 0.3646789	+ 0.0185178	14.8	- 0.3229008	+ 0.0316683
11.9	+ 0.3610210	+ 0.0545247	14.9	- 0.3244424	- 0.0008300
12.0	+ 0.3538020	+ 0.0896913	15.0	- 0.3227425	- 0.0331024
12.1	+ 0.3431221	+ 0.1236796	15.1	- 0.3178400	- 0.0648324
12.2	+ 0.3291161	+ 0.1561661	15.2	- 0.3098044	- 0.0957100
12.3	+ 0.3119493	+ 0.1868435	15.3	- 0.2987362	- 0.1254361
12.4	+ 0.2918171	+ 0.2154260	15.4	- 0.2847652	- 0.1537247
12.5	+ 0.2689428	+ 0.2416485	15.5	- 0.2680484	- 0.1803057
12.6	+ 0.2435740	+ 0.2652730	15.6	- 0.2487694	- 0.2049274
12.7	+ 0.2159819	+ 0.2860869	15.7	- 0.2271358	- 0.2273390
12.8	+ 0.1864566	+ 0.3039080	15.8	- 0.2033775	- 0.2473930
12.9	+ 0.1553051	+ 0.3185840	15.9	- 0.1777434	- 0.2648464
13.0	+ 0.1228486	+ 0.3299950	16.0	- 0.1504996	- 0.2795630

## (B.)

From the simple relation between the  $G$ ,  $J$ , and  $Y$  functions, viz.

$$Y_n(x) = (\log 2 - \gamma)J_n(x) - G_n(x),$$

the values of the Neumann functions  $Y_0(x)$  and  $Y_1(x)$  are readily obtained. Tables of the functions were calculated to four places of decimals by Smith with a possible error of two in the last figure\*.

For interpolation purposes, formulæ similar to those for  $G_0(x)$  and  $G_1(x)$  may be used.

\* Smith, Messenger of Mathematics, 1897.

TABLE II.  
Greatest error .0000001.

$x$ .	$Y_0(x)$ .	$Y_1(x)$ .	$x$ .	$Y_0(x)$ .	$Y_1(x)$ .
0.1	- 2.2943346	-10.1399073	5.1	- 0.5219048	+ 0.1395766
0.2	- 1.5834212	- 5.2095168	5.2	- 0.5331139	+ 0.0846015
0.3	- 1.1547248	- 3.5848063	5.3	- 0.5388333	+ 0.0298674
0.4	- 0.8406008	- 2.7746616	5.4	- 0.5391120	- 0.0241284
0.5	- 0.5894502	- 2.2832969	5.5	- 0.5340483	- 0.0769028
0.6	- 0.3788761	- 1.9465804	5.6	- 0.5237877	- 0.1279898
0.7	- 0.1973369	- 1.6948399	5.7	- 0.5085214	- 0.1769452
0.8	- 0.0382373	- 1.4937049	5.8	- 0.4884837	- 0.2233504
0.9	+ 0.1024584	- 1.3244417	5.9	- 0.4639494	- 0.2668153
1.0	+ 0.2273442	- 1.1761105	6.0	- 0.4352307	- 0.3069820
1.1	+ 0.3381522	- 1.0420112	6.1	- 0.4026739	- 0.3435269
1.2	+ 0.4360782	- 0.9179113	6.2	- 0.3666552	- 0.3761647
1.3	+ 0.5219762	- 0.8010938	6.3	- 0.3275793	- 0.4046482
1.4	+ 0.5964808	- 0.6898135	6.4	- 0.2858710	- 0.4287732
1.5	+ 0.6600864	- 0.5829705	6.5	- 0.2419754	- 0.4483766
1.6	+ 0.7132005	- 0.4799054	6.6	- 0.1963504	- 0.4633398
1.7	+ 0.7561814	- 0.3802657	6.7	- 0.1494645	- 0.4735886
1.8	+ 0.7893631	- 0.2839159	6.8	- 0.1017897	- 0.4790933
1.9	+ 0.8130747	- 0.1908736	6.9	- 0.0538035	- 0.4798680
2.0	+ 0.8276522	- 0.1012656	7.0	- 0.0059732	- 0.4759716
2.1	+ 0.8334489	- 0.0152936	7.1	+ 0.0412383	- 0.4675041
2.2	+ 0.8308405	+ 0.0667906	7.2	+ 0.0873798	- 0.4546088
2.3	+ 0.8202297	+ 0.1447052	7.3	+ 0.1320184	- 0.4374672
2.4	+ 0.8020483	+ 0.2181536	7.4	+ 0.1747389	- 0.4162989
2.5	+ 0.7767579	+ 0.2868366	7.5	+ 0.2151524	- 0.3913585
2.6	+ 0.7448496	+ 0.3504635	7.6	+ 0.2528949	- 0.3629333
2.7	+ 0.7068429	+ 0.4087597	7.7	+ 0.2876333	- 0.3313388
2.8	+ 0.6632837	+ 0.4614743	7.8	+ 0.3190683	- 0.2969186
2.9	+ 0.6147415	+ 0.5083855	7.9	+ 0.3469349	- 0.2600377
3.0	+ 0.5618064	+ 0.5493050	8.0	+ 0.3710065	- 0.2210791
3.1	+ 0.5050853	+ 0.5840829	8.1	+ 0.3910948	- 0.1804440
3.2	+ 0.4451982	+ 0.6126099	8.2	+ 0.4070530	- 0.1385432
3.3	+ 0.3827739	+ 0.6348198	8.3	+ 0.4187751	- 0.0957947
3.4	+ 0.3184456	+ 0.6506912	8.4	+ 0.4261976	- 0.0526205
3.5	+ 0.2528462	+ 0.6602489	8.5	+ 0.4292992	- 0.0094419
3.6	+ 0.1866039	+ 0.6635634	8.6	+ 0.4281000	+ 0.0333237
3.7	+ 0.1203377	+ 0.6607516	8.7	+ 0.4226621	+ 0.0752684
3.8	+ 0.0546525	+ 0.6519762	8.8	+ 0.4130871	+ 0.1159960
3.9	- 0.0098635	+ 0.6374438	8.9	+ 0.3995159	+ 0.1551257
4.0	- 0.0726527	+ 0.6174037	9.0	+ 0.3821269	+ 0.1922965
4.1	- 0.1331723	+ 0.5921463	9.1	+ 0.3611334	+ 0.2271690
4.2	- 0.1909188	+ 0.5619996	9.2	+ 0.3367803	+ 0.2594298
4.3	- 0.2454214	+ 0.5273274	9.3	+ 0.3093440	+ 0.2887952
4.4	- 0.2962467	+ 0.4885254	9.4	+ 0.2791264	+ 0.3150089
4.5	- 0.3430029	+ 0.4460183	9.5	+ 0.2464545	+ 0.3378498
4.6	- 0.3853418	+ 0.4002555	9.6	+ 0.2116746	+ 0.3571306
4.7	- 0.4229611	+ 0.3517075	9.7	+ 0.1751518	+ 0.3727008
4.8	- 0.4556067	+ 0.3008619	9.8	+ 0.1372627	+ 0.3844449
4.9	- 0.4830736	+ 0.2482186	9.9	+ 0.0983933	+ 0.3922882
5.0	- 0.5052074	+ 0.1942862	10.0	+ 0.0589363	+ 0.3961925

TABLE II. (continued).

$x$ .	$Y_0(x)$ .	$Y_1(x)$ .	$x$ .	$Y_0(x)$ .	$Y_1(x)$ .
10.1	+ 0.0192732	+ 0.3961587	13.1	- 0.0647374	- 0.3437170
10.2	- 0.0201652	+ 0.3922239	13.2	- 0.0302316	- 0.3458431
10.3	- 0.0590321	+ 0.3844657	13.3	+ 0.0043165	- 0.3445304
10.4	- 0.0969345	+ 0.3729956	13.4	+ 0.0385241	- 0.3398172
10.5	- 0.1335114	+ 0.3579606	13.5	+ 0.0721689	- 0.3317752
10.6	- 0.1684138	+ 0.3395406	13.6	+ 0.1048094	- 0.3205080
10.7	- 0.2013136	+ 0.3179468	13.7	+ 0.1361673	- 0.3061498
10.8	- 0.2319054	+ 0.2934192	13.8	+ 0.1659418	- 0.2888644
10.9	- 0.2599086	+ 0.2662248	13.9	+ 0.1938491	- 0.2688437
11.0	- 0.2850720	+ 0.2366520	14.0	+ 0.2196265	- 0.2463027
11.1	- 0.3071704	+ 0.2050143	14.1	+ 0.2430335	- 0.2214829
11.2	- 0.3260159	+ 0.1716369	14.2	+ 0.2638557	- 0.1946443
11.3	- 0.3414512	+ 0.1368628	14.3	+ 0.2819044	- 0.1660660
11.4	- 0.3533537	+ 0.1010433	14.4	+ 0.2970207	- 0.1360404
11.5	- 0.3616369	+ 0.0645397	14.5	+ 0.3090745	- 0.1048760
11.6	- 0.3662508	+ 0.0277148	14.6	+ 0.3179684	- 0.0728858
11.7	- 0.3671814	- 0.0090675	14.7	+ 0.3236352	- 0.0403916
11.8	- 0.3644508	- 0.0454469	14.8	+ 0.3260405	- 0.0077174
11.9	- 0.3581170	- 0.0810711	14.9	+ 0.3251834	+ 0.0248135
12.0	- 0.3482733	- 0.1155959	15.0	+ 0.3210934	+ 0.0568804
12.1	- 0.3350455	- 0.1486917	15.1	+ 0.3138332	+ 0.0881706
12.2	- 0.3185930	- 0.1800459	15.2	+ 0.3034953	+ 0.1183799
12.3	- 0.2991043	- 0.2093642	15.3	+ 0.2902029	+ 0.1472173
12.4	- 0.2767969	- 0.2363760	15.4	+ 0.2741069	+ 0.1744069
12.5	- 0.2519143	- 0.2608333	15.5	+ 0.2553851	+ 0.1996910
12.6	- 0.2247227	- 0.2825169	15.6	+ 0.2342402	+ 0.2228318
12.7	- 0.1955098	- 0.3012348	15.7	+ 0.2108972	+ 0.2436150
12.8	- 0.1645802	- 0.3168264	15.8	+ 0.1856022	+ 0.2618487
12.9	- 0.1322530	- 0.3291626	15.9	+ 0.1586181	+ 0.2773702
13.0	- 0.0988593	- 0.3381471	16.0	+ 0.1302233	+ 0.2900429

LXIV. *The Problem of Partition of Energy, especially in Radiation.* By Prof. W. PEDDIE\*.

1. **A**GREEMENT seems to be nearly as remote as ever regarding the manner in which deviation from the condition of equipartition of energy amongst the various freedoms of an apparently conservative system, in apparent statistical equilibrium, is brought about. The well-known discrepancies which occur between the actual ratios of the principal specific heats of gases and their theoretical ratios calculated, on the assumption of equipartition, from the multiplicity of freedoms which radiational phenomena make evident

\* Communicated by the Author.

in the case of even monatomic gases, make the fact of extreme deviation from equipartition very evident.

It is fully recognized that, in very many special cases, dynamical freedoms may be entirely inoperative. So one way of avoiding the difficulty consists in asserting that the special freedoms made evident in radiational phenomena are inoperative in ordinary thermal phenomena. Such a mode is unsatisfactory apart from the specification, by analogy at least, of an appropriate mechanism ; for the doctrine of equipartition does not permit mere partial inoperativeness—the inoperativeness must be total. Another method, adopted by Jeans, consists in regarding a final condition of statistical equilibrium between matter and æther, with consequent equipartition of energy amongst the freedoms, as unattainable in finite time ; so that the practical “steady” conditions, which subsist in experimental tests, and are the result of a steady supply of energy in one form compensating an equal steady loss in another form, give rise to that non-equable partitioning of energy amongst wave-lengths which is expressed by Planck’s well-corroborated law. A third method, that of Planck, locates the source of non-equipartition in the intrinsic nature of energy itself, which is postulated to be atomic, the ultimate unit being so large that it may only be manifested in relation to many degrees of freedom, some freedoms absorbing no units, others one, and so on.

2. Planck’s postulate has the merit of leading to a well supported expression for the distribution of energy amongst the various wave-lengths in “natural” radiation ; it has the possible demerit of necessitating discontinuities of motion on molecular, atomic, or, at any rate, on “freedomal” scale. Yet it may be that the seeming demerit is not real, the discontinuities vanishing as a matter of statistics.

Sir J. Larmor, in his recent Bakerian Lecture (Proc. R. S. 1909, vol. lxxxiii.) modifies and amplifies Planck’s treatment in such a way as to get rid of the assumption of the finitely atomic nature of energy. Indivisibility of an element of energy is replaced by an unalterable ratio of the element of energy of any one type to the extent of a “cell,” of corresponding type, in which that element is contained. The actual element itself may be infinitesimal ; so motional discontinuities become infinitesimal. A “cell” replaces the “degree of freedom” of the previous treatment, and each cell is of equal opportunity or extent as regards an element of disturbance, which may pass from one cell to another of a different type, the amount of energy associated with it being

possibly altered in the process. Thus—in analogy with the passage of heat energy in diminished (or increased) amount from a region of high to one of low temperature (or conversely), in association with the necessary performance (or absorption) of external work—we have the transformation of radiation from one wave-length to another in association with the performance or absorption of work. The disturbance has equal opportunities for the occupation of each cell. These postulates lead to Planck's law, the constants only having important modifications of meaning.

3. Jeans has recently discussed Larmor's view, and arrives at the conclusion (*Phil. Mag.* Dec. 1910) that it is neither possible to avoid finiteness of the element of energy nor ultimate discontinuity of æther structure in relation to radiation if Planck's law corresponds to the true final condition of equilibrium. That is to say, radiation can only be regarded as capable of existing in the æther in amounts which are multiples of a finite unit.

While Jeans's own view (§ 1) must be recognized as indicating a possible solution of the fundamental difficulty regarding the partition of energy, it is not possible, because of our ignorance of the intrinsic nature of matter, of æther, and of the connexion between these, to be quite certain that Larmor's view, or even Planck's, is inadmissible. It is perhaps not impossible that the nature of these entities may impose identity between the distribution which obtains in the steady state under experimental conditions and that which would obtain in the final state of a strictly conservative self-contained system. I therefore venture to indicate the following mode of considering the problem. It leads to an expression which differs slightly in form from that of Planck, but which can practically be identified with it throughout the range of observed wave-lengths, and which, with it, reduces to Rayleigh's form when the wave-length is of suitable magnitude.

4. Interchange of energy amongst freedoms of the same type constitutes ordinary transmission of energy of the type involved; interchange of energy amongst freedoms of distinct types constitutes that transmission of energy which is ordinarily called transformation. When different sub-systems, in the equilibrium condition, are freely open to interchanges of energy, a universal generalized temperature or potential, possessing a definite statistical value throughout the total system when that system possesses a definite total amount of energy, must exist.

Let there be altogether  $\nu$  subsystems, let  $N_1 \dots N_\nu$  be the numbers of freedoms in each subsystem, and let  $c_1 \dots c_\nu$  be the capacities of the subsystems for energy. If  $P$  be the equilibrium value of the universal potential, the amounts of energy,  $E_1 \dots E_\nu$ , in each subsystem are  $c_1 P, \dots c_\nu P$  respectively. As in Boltzmann's treatment, the equilibrium state is the most probable state; and so, following Planck's modification of that treatment, the probability being estimated by the number of ways in which  $cP$  units of energy can be contained in  $N$  freedoms, we obtain, as the condition of equilibrium, the equation

$$\sum_1^\nu {}^m \log \frac{N_m + c_m P}{c_m P} \partial \cdot c_m P = 0. \dots \dots (1)$$

Now, in the condition of statistical equilibrium, as in the approach to it, there is constant transmission of energy from one subsystem to another; and the energy tends to accumulate in those subsystems from which the rate of transmission is slowest. Hence the total rate of transmission tends to a minimum. So  $r_m c_m P$  being the rate of transmission from the subsystem  $m$ , we have, if the  $r$ 's are constant,

$$\sum_1^\nu {}^m r_m \partial \cdot c_m P = 0. \dots \dots (2)$$

These two equations imply nothing more regarding the potential  $P$  than that it is statistically uniform throughout the total system. It might be slowly varying with time. If we further add the condition of conservation of energy, we get

$$\sum_1^\nu {}^m \partial \cdot c_m P = 0. \dots \dots (3)$$

The three equations give

$$E_m = c_m P = \frac{N_m}{e^{a+br_m} - 1}, \dots \dots (4)$$

where  $a$  and  $b$  are functions of  $P$  alone. The simplest admissible conditions are  $a = \alpha P^{-1}$ ,  $b = \beta P^{-1}$ , where  $\alpha$  and  $\beta$  are absolute constants, in which case (4) becomes

$$E_m = c_m P = \frac{N_m}{e^{\frac{\alpha + \beta r_m}{P}} - 1} \dots \dots (4')$$

5. To apply this expression to the case of radiation we have to evaluate  $E_{mr_m} = E_\lambda$ , the energy transmitted per second per unit range of wave-length in the neighbourhood of wave-length  $\lambda$ . We must therefore either appeal to experiment for the determination of the appropriate forms to be given to  $N_m$  and  $r_m$  in terms of  $\lambda$ , or we must determine these by means of suitable assumptions regarding æther and matter and their connexion. Thus if we assume that the fractional rate of transmission of the energy content of each freedom is identical per vibration, the fractional rate of transmission per unit of time is proportional to the frequency, so that we can write  $\beta r_m = \gamma \lambda^{-1}$ ,  $\gamma$  being an absolute constant. The value of  $N_m$ , when the frequency is not too small, is given by Rayleigh's reasoning (Sc. Papers, vol. iv. p. 484, or Phil. Mag. xlix. p. 539, 1900) as  $A\lambda^{-4}$ , where  $A$  is a universal constant. Hence

$$E_\lambda = \frac{A\lambda^{-5}}{\epsilon^{\frac{\alpha + \gamma\lambda^{-1}}{P}} - 1}, \dots \dots \dots (5)$$

an expression which, with Wien's displacement law holding, gives the well-known experimental result that the maximum energy is proportional to the fifth power of the absolute temperature provided that the latter be identified with  $P$ . The expression becomes identical with Planck's if we put  $\alpha = 0$ ; it is practically identical with Planck's so long as  $\alpha\lambda$  is negligible relatively to  $\gamma$ . We must therefore recognize that this restriction holds throughout the range of wave-length to which Planck's formula is applicable. Outside that range the quantity  $E_\lambda$  becomes very small.

If within that range  $P\lambda$  becomes large relatively to  $\gamma$ , the expression (5) reduces to  $A\gamma^{-1} \cdot P\lambda^{-4}$ , which is the form given by Rayleigh as applicable when  $P\lambda$  is sufficiently large while  $\lambda$  is not too large. When  $\lambda$  is very large with  $P$  not too small, (5) takes the form  $A\alpha^{-1} \cdot P\lambda^{-5}$ .

6. The distinction between energy transmitted by, and energy stored in, definite freedoms is of fundamental importance. Thus (4') shows that there is not universal equipartition of the energy allotted to all freedoms except under the condition that  $\beta r_m$  is negligible relatively to  $\alpha$ ; while, on the other hand, there is equipartition universally amongst the energies transmitted per unit of time if  $\beta r_m$  is large relatively to  $\alpha$  and small relatively to  $P$ .

The ratio of the energy transmitted per unit of time per degree of freedom to the energy stored in that freedom takes here the place of the element of energy, and there is no limitation upon its finitude. There is necessarily equipartition of energy amongst all freedoms for which that ratio has one and the same value.

LXV. *Supplemental Note on a Proposed Method for the better practical application of Fourier's Theorem.* By L. R. MANLOVE \*.

THE method suggested by the writer in the *Phil. Mag.* for July last involves this assumption :—

“ When, being uncertain whether there are any real roots of an equation between two given consecutive integers, we proceed as if approximating by Lagrange's method to the roots in that interval, then in case no such roots actually exist we shall ultimately obtain a derivative equation which can be seen to have unity for the superior limit of its positive roots.”

No formal proof is attempted, but the following considerations show that the assumption is well founded.

*Ex hypothesi* we have a series of derivative equations none of which has a positive root greater than unity, and for the present purpose we may treat these as independent equations.

Given that an equation has in fact no real root greater than unity, and that nothing further is known, what is the probability that it can be seen to have unity as a superior limit of the roots?

Suppose that this probability is  $p$  for each equation ; then the probability of the first equation failing is  $1-p$  ; and the probability of the first  $n$  equations all failing is  $(1-p)^n$  which may be made as small a quantity as we please by taking  $n$  large enough.

In testing the method with some scores of examples the writer has only in one case found it necessary to go so far as the 3rd derivative equation. Of forty equations taken at random only five required more than one derivative to clear up an interval.

\* Communicated by the Author.



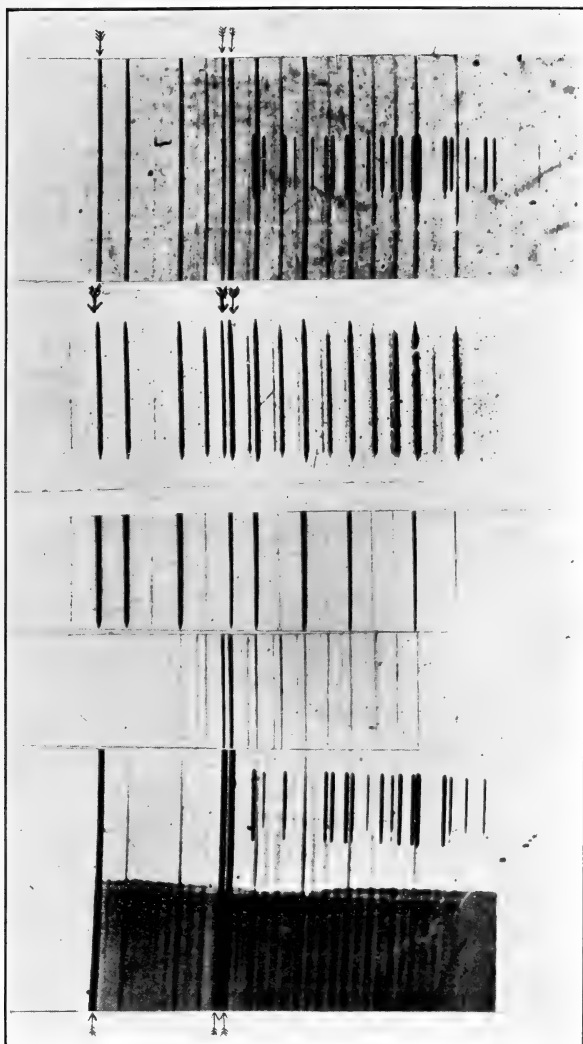


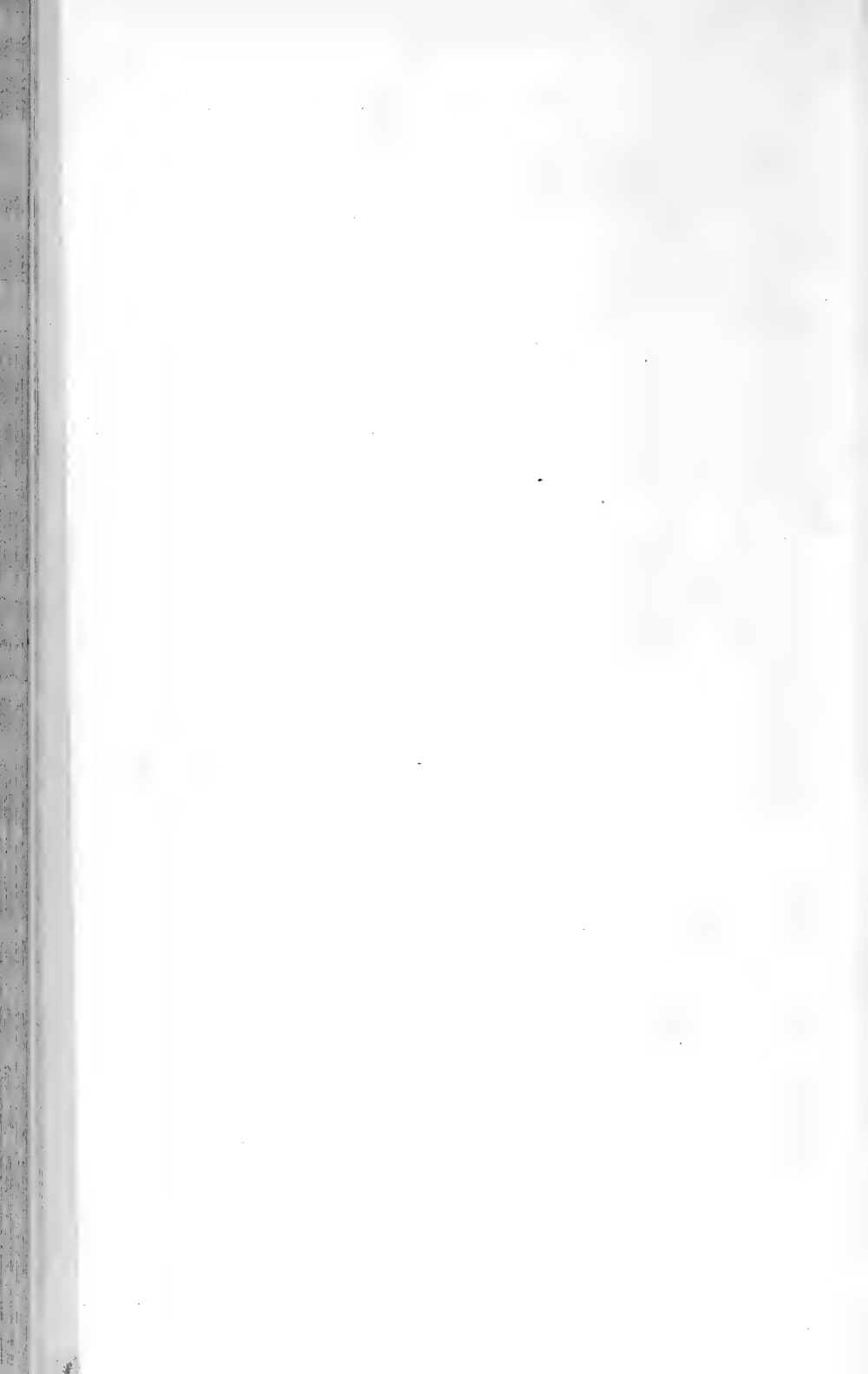
FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

FIG. 5.



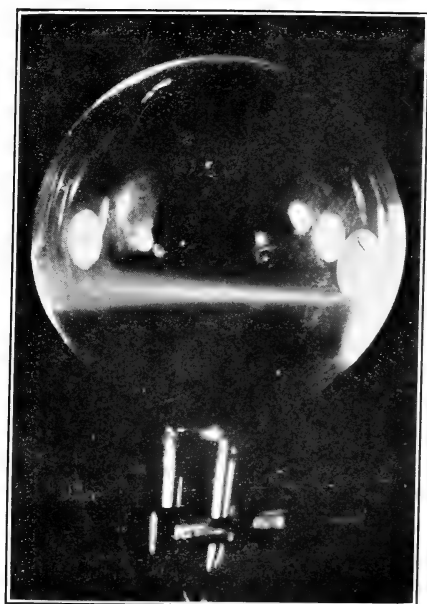


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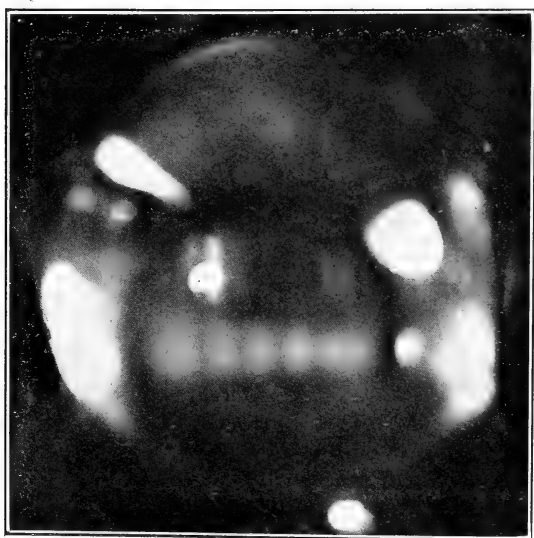


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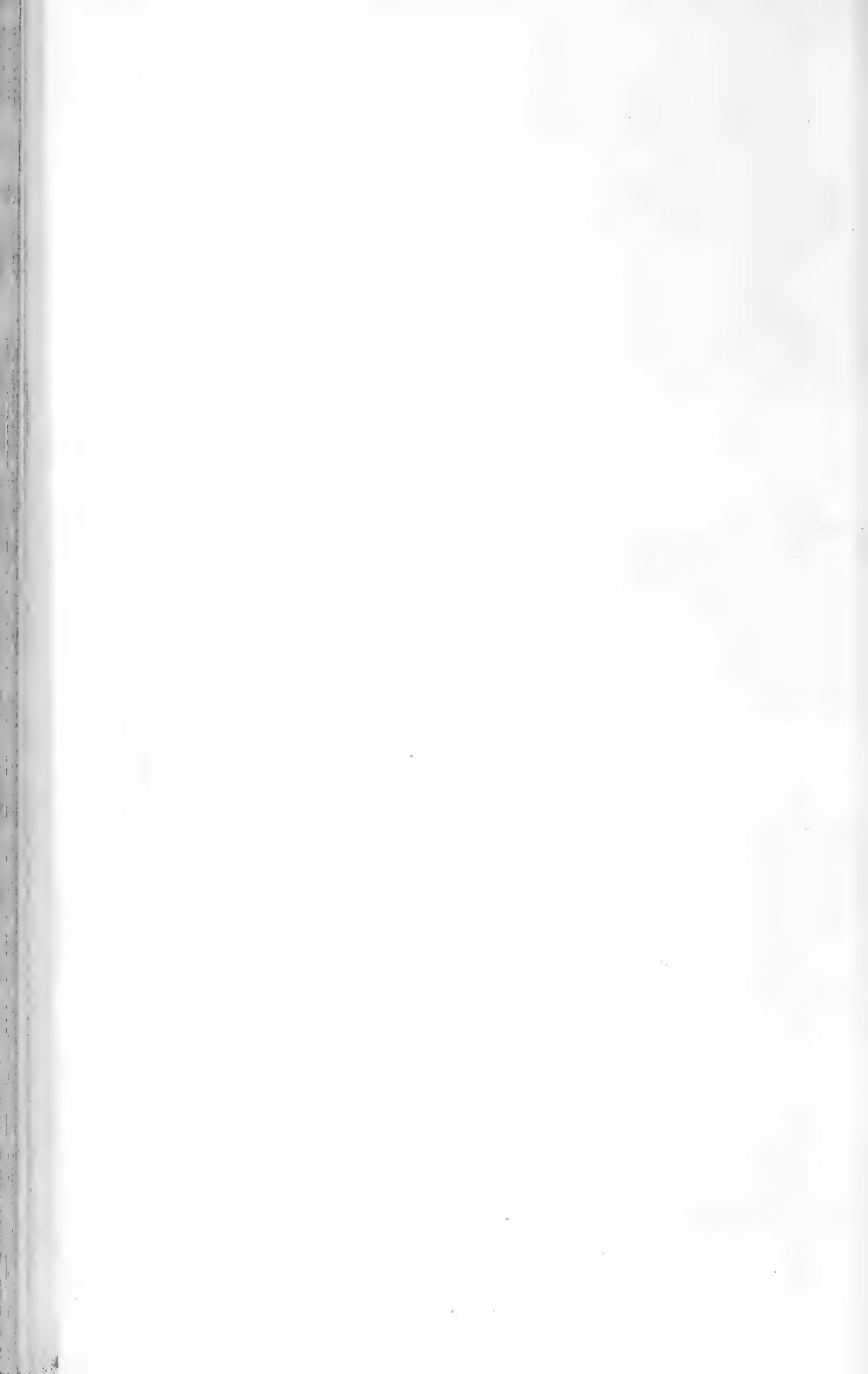


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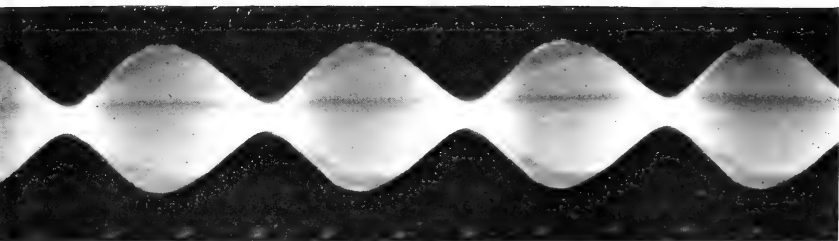


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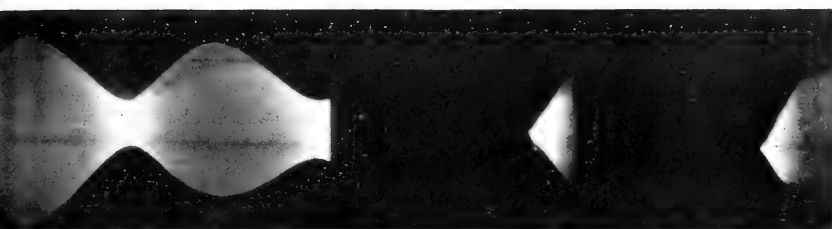


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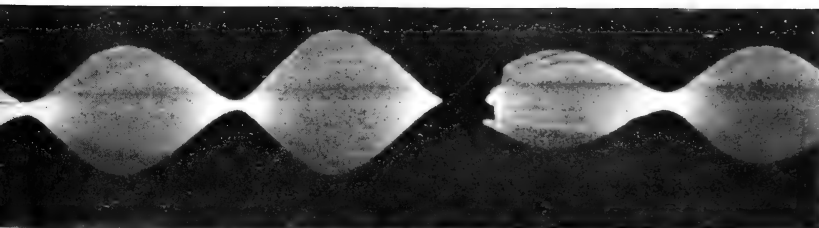


FIG. 5.

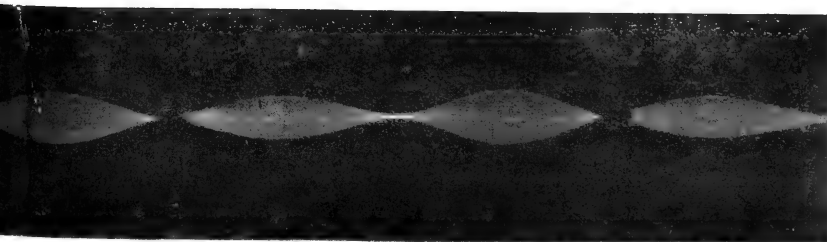




FIG. 9.

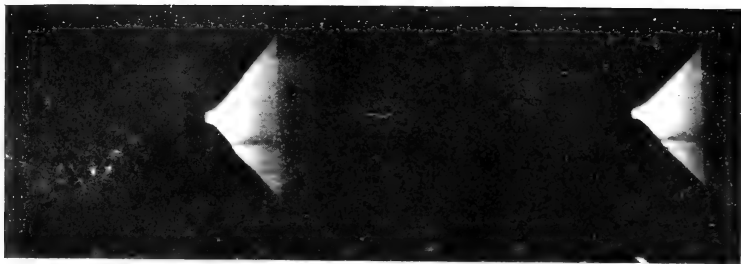


FIG. 10.

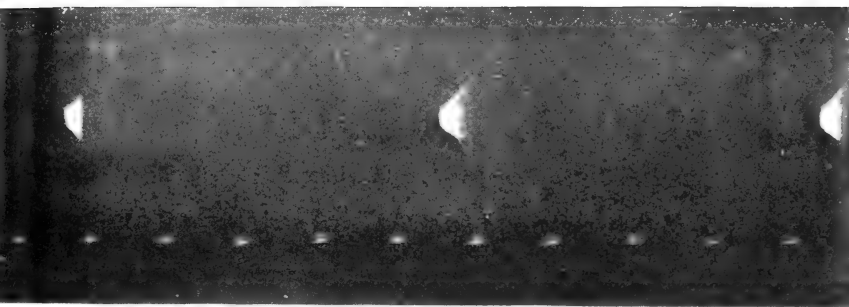


FIG. 11.

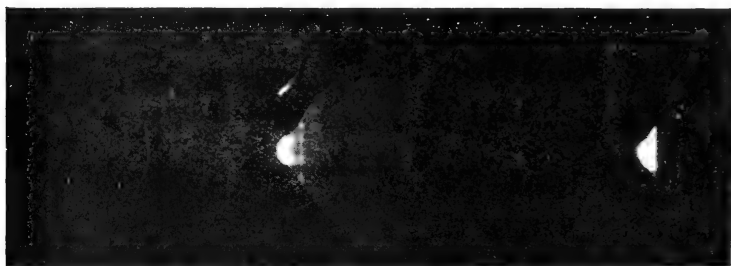
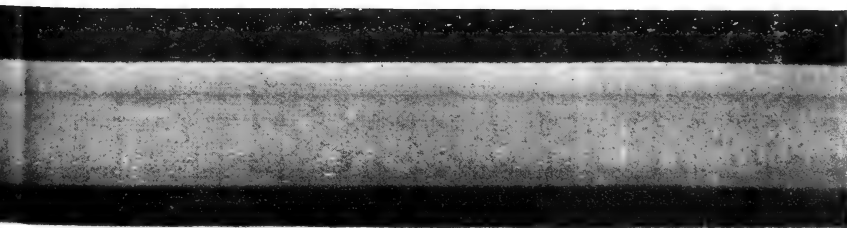


FIG. 14.



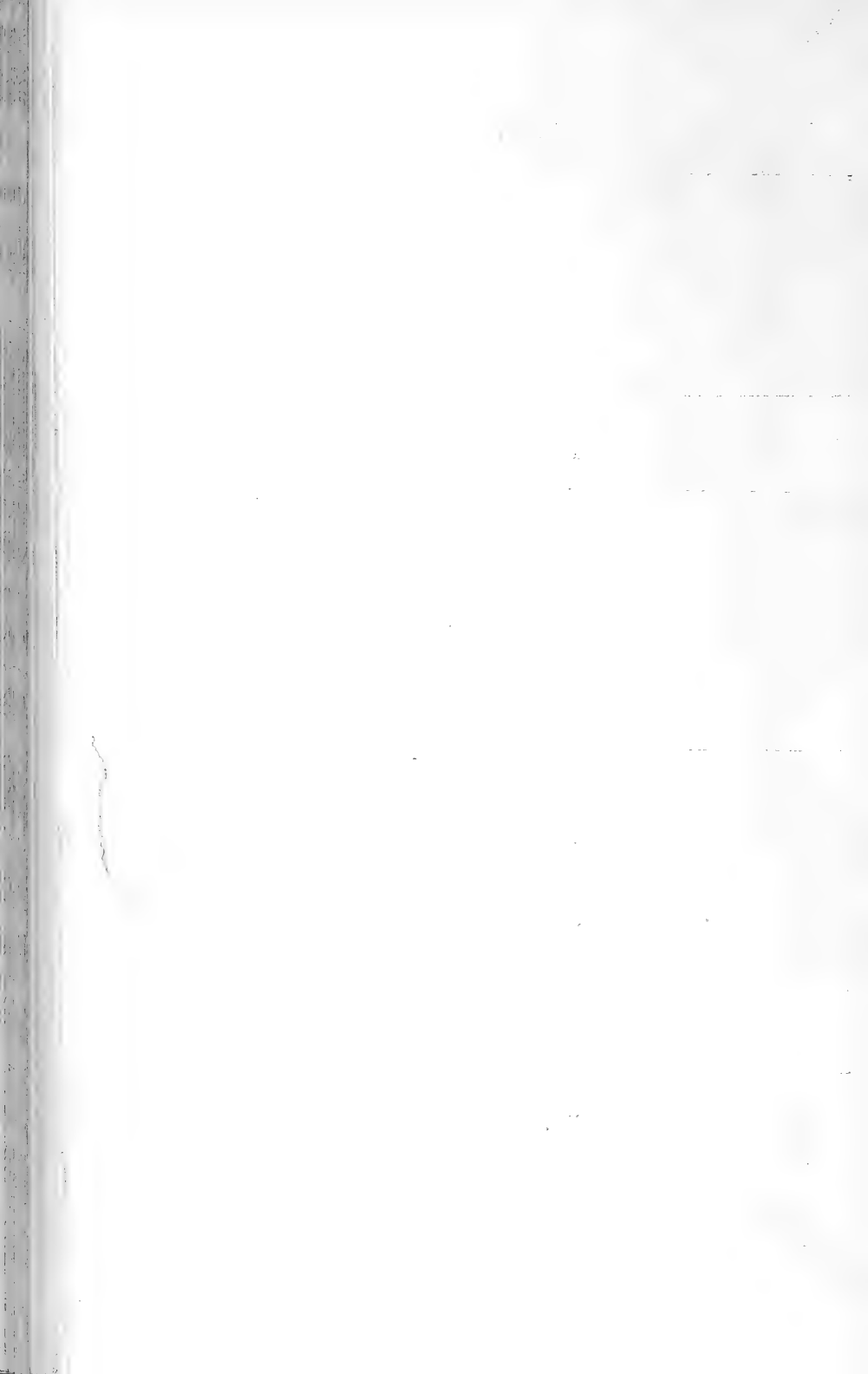




FIG. 18.

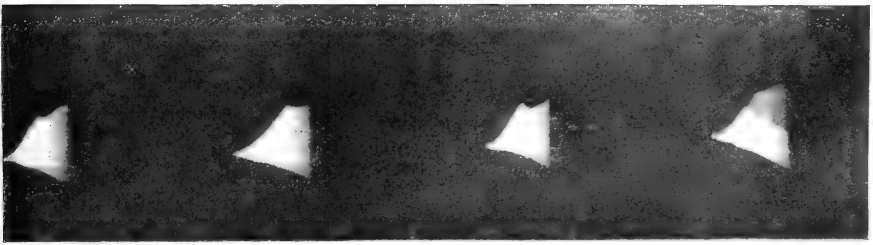


FIG. 19.

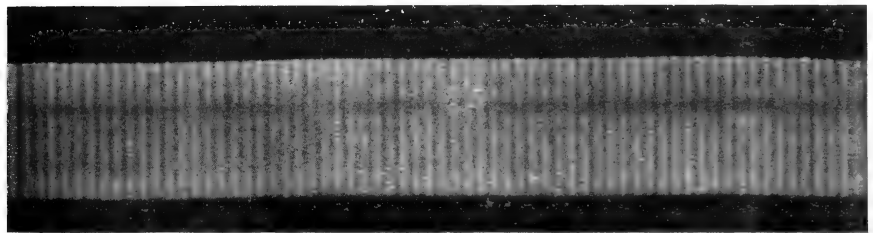


FIG. 20.

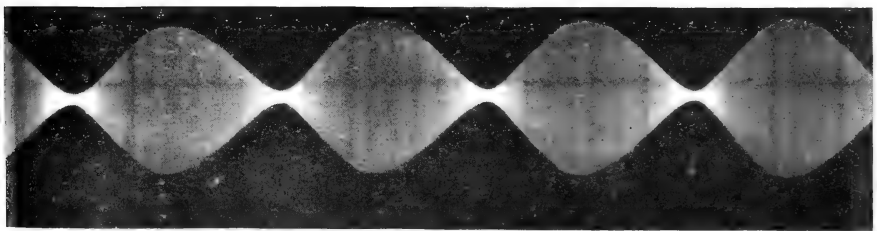
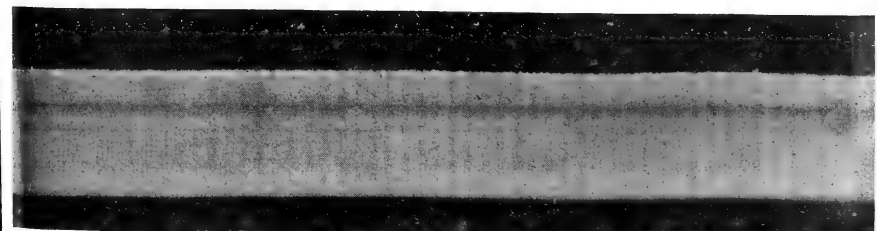


FIG. 21.



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FIG. 2.

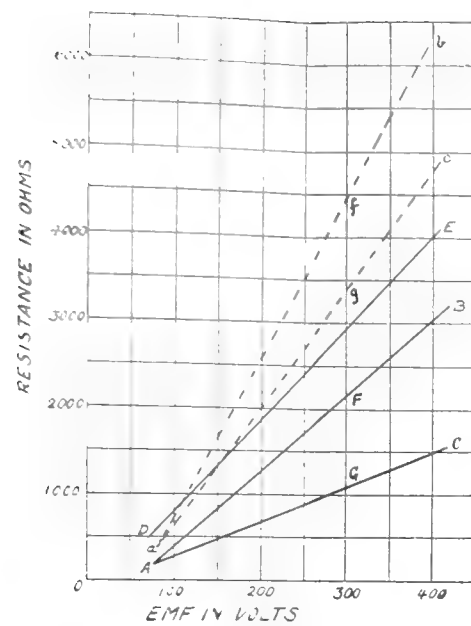


FIG. 7.

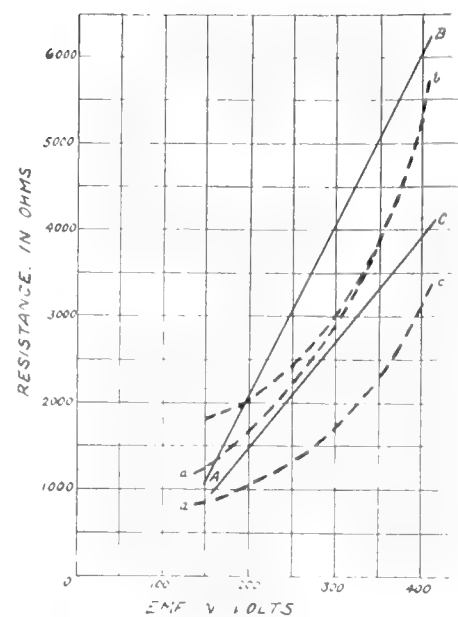


FIG. 13.

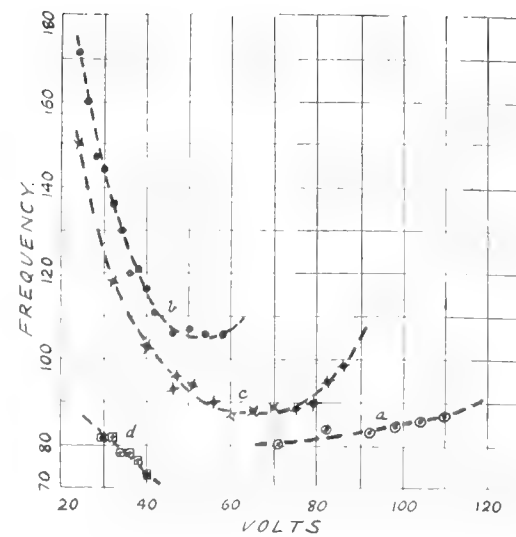


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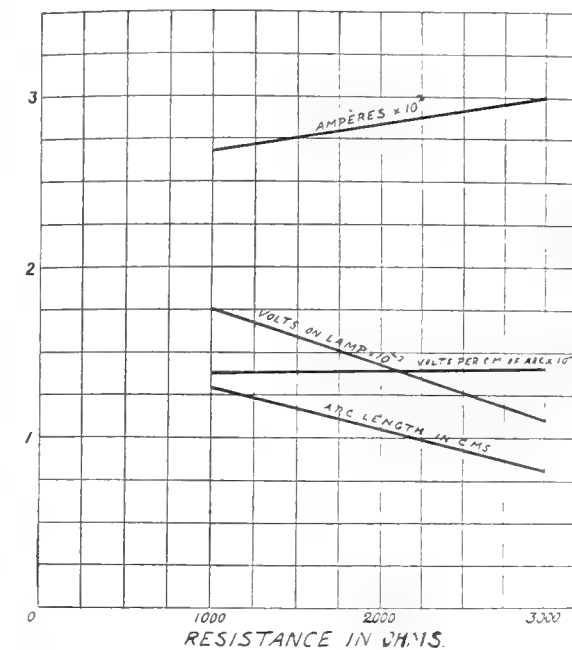


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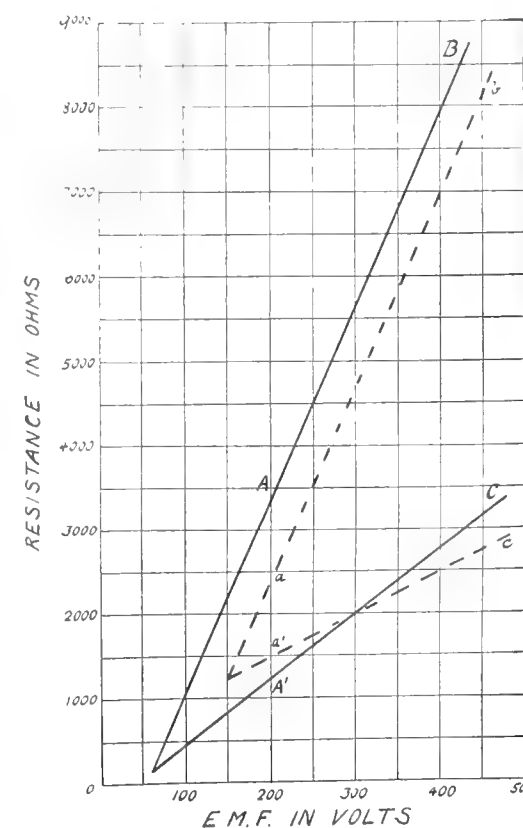


FIG. 6.

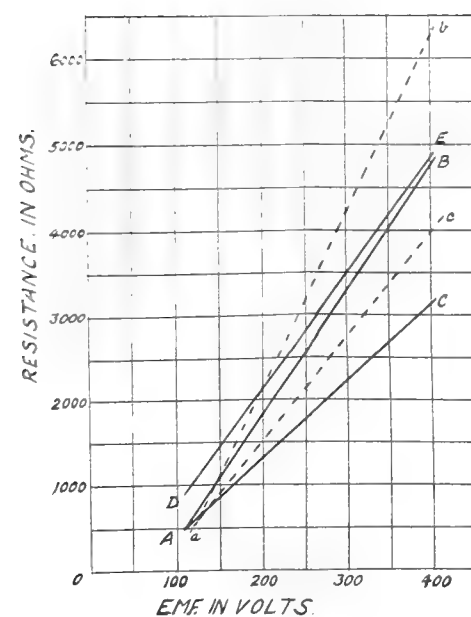


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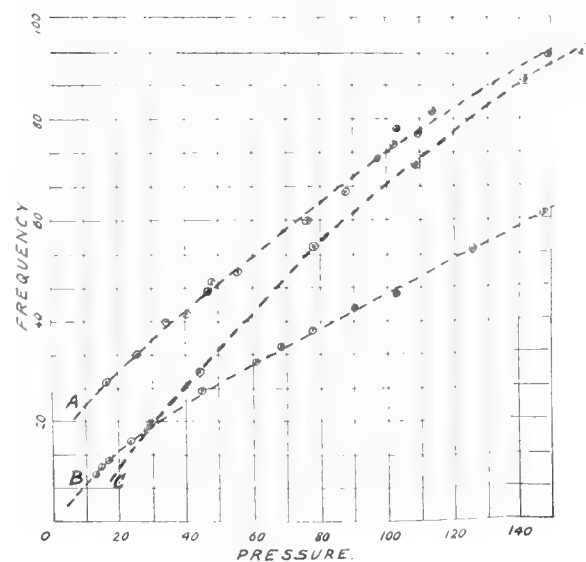


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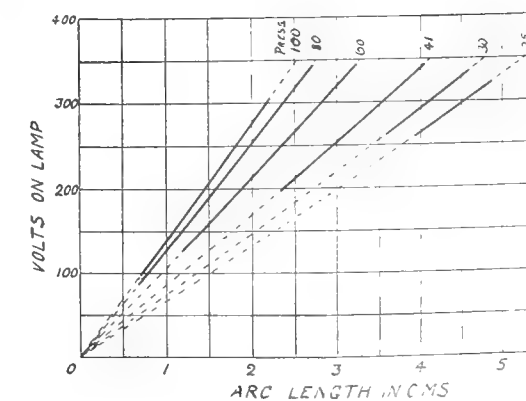










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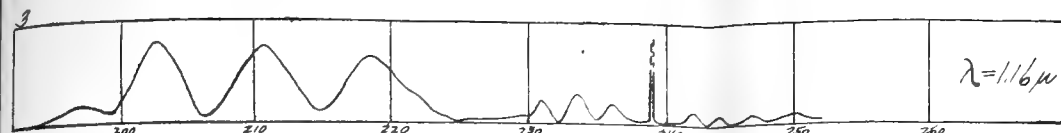


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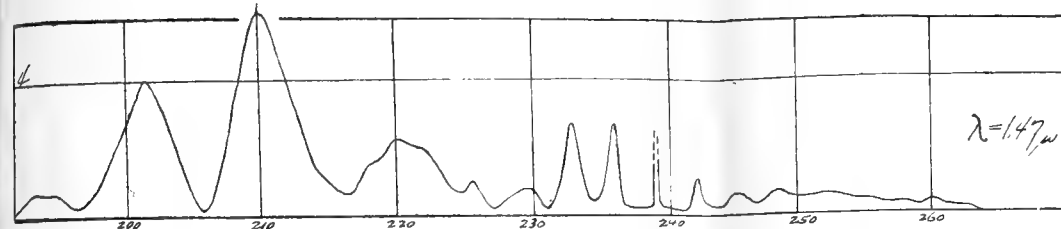


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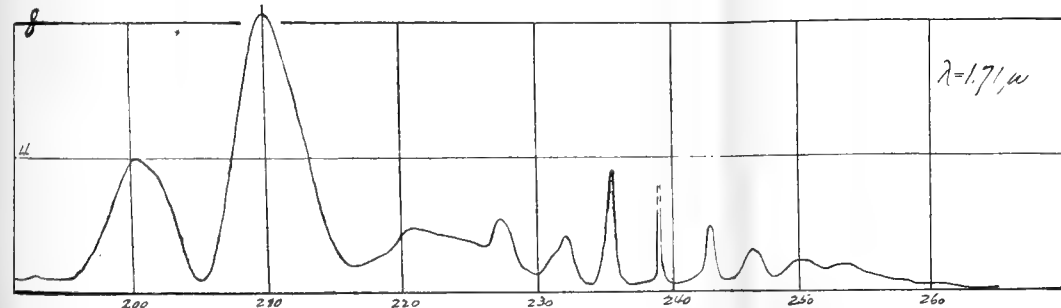


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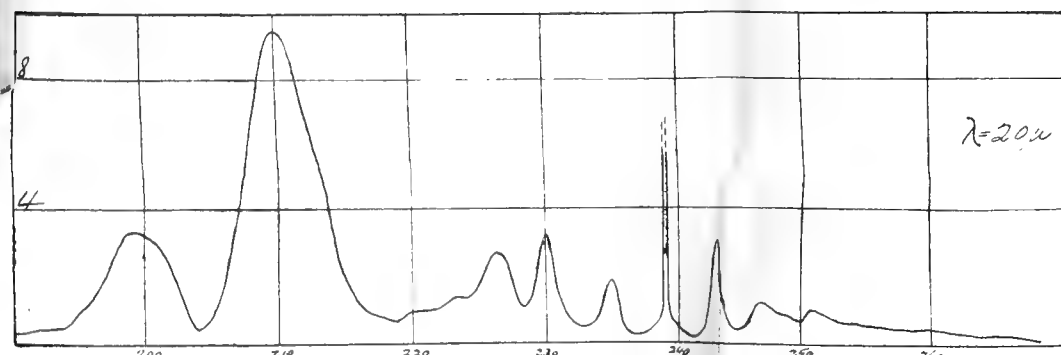


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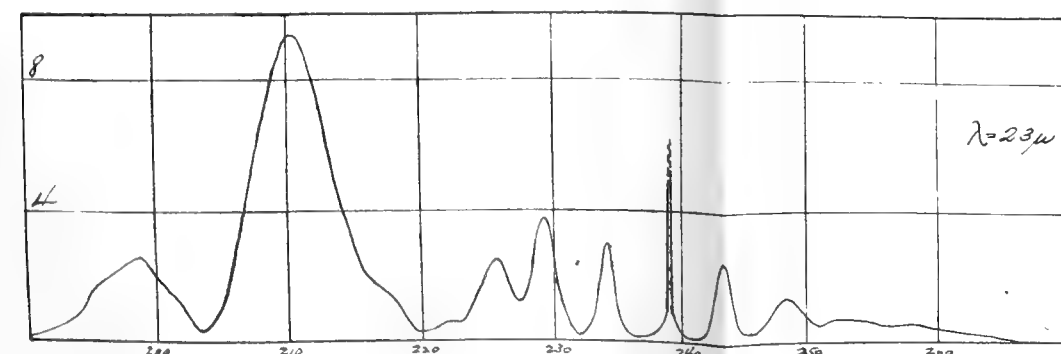


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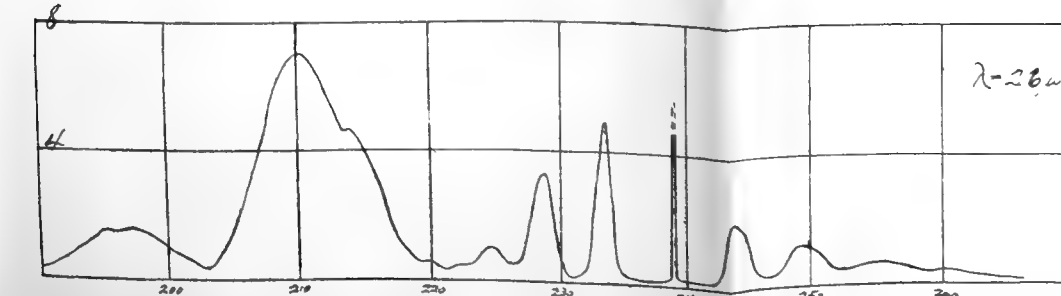


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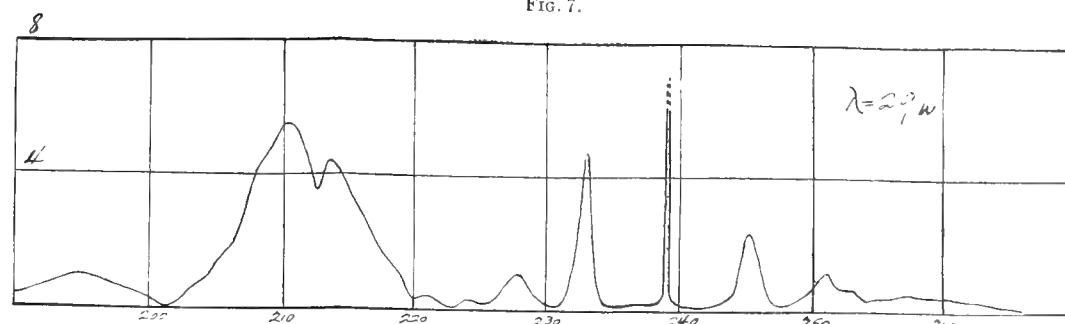


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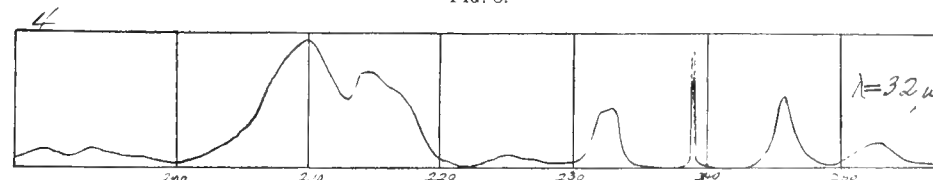


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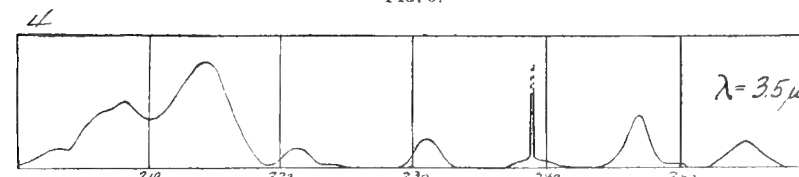


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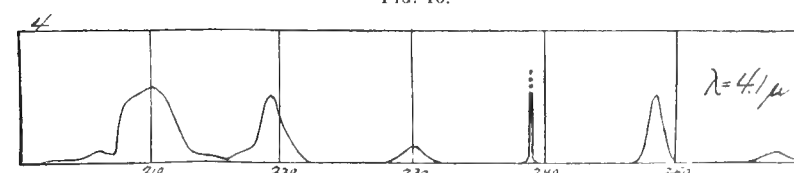


FIG. 11.

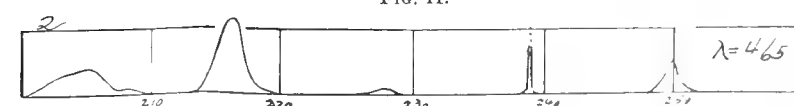
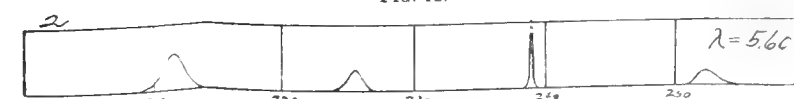


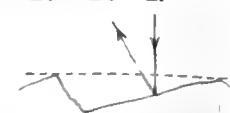
FIG. 12.

**WOOD GRATING No. 6.**

GRATING SPACE: 00123 cm.

ANGLE BETWEEN COLLIMATORS:  $2\theta = 25^\circ.2$ .

Form of Groove (Approximate).



1000





FIG. 1.

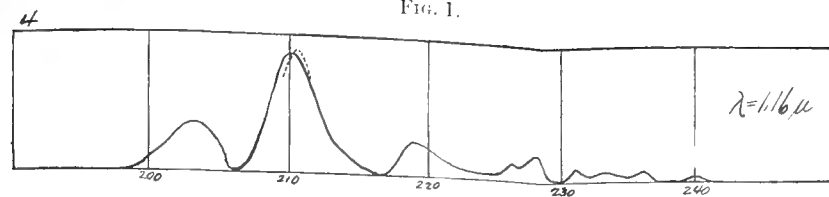


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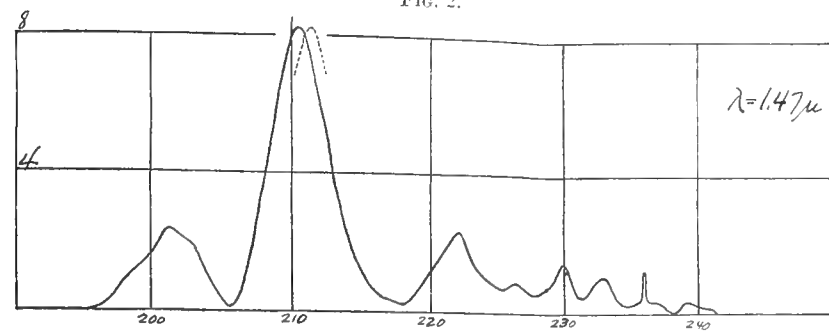


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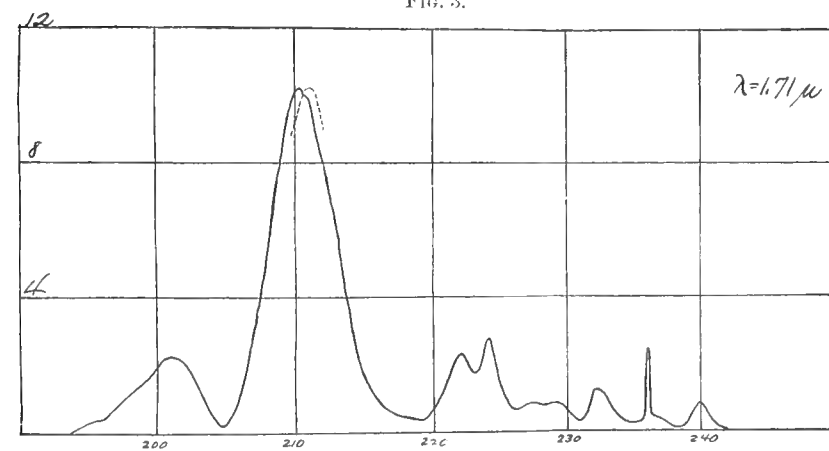


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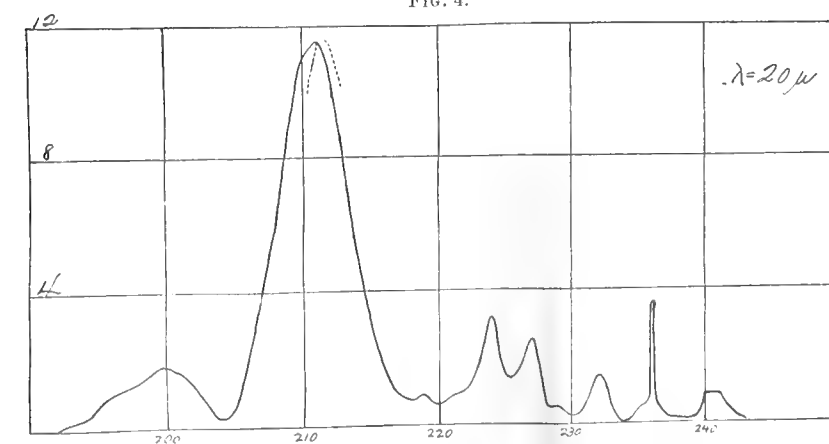


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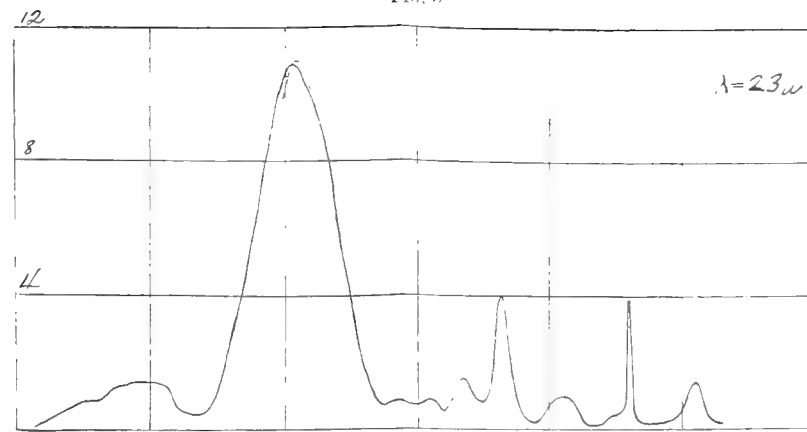


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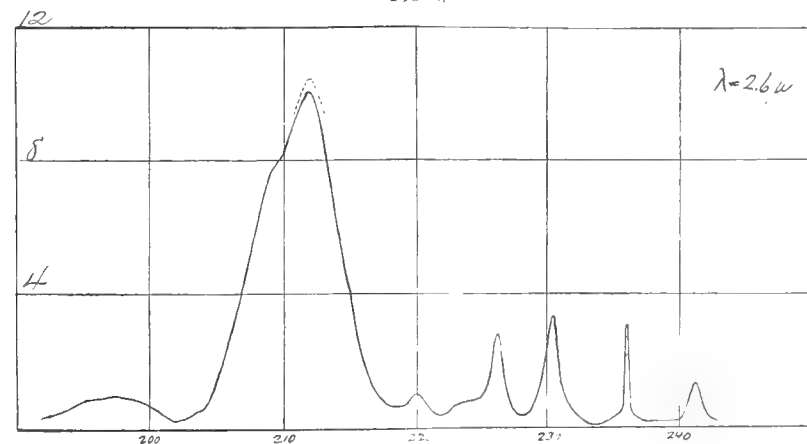


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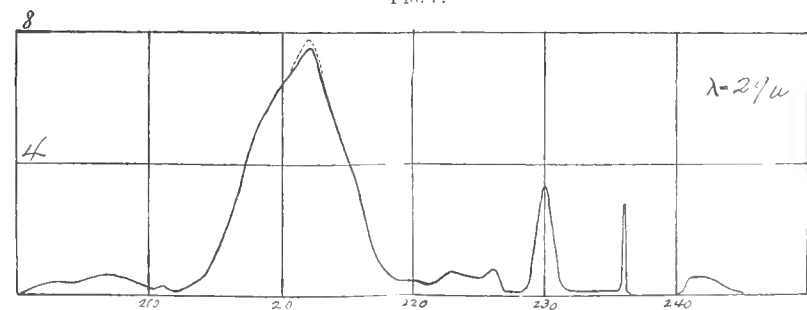


FIG. 8.

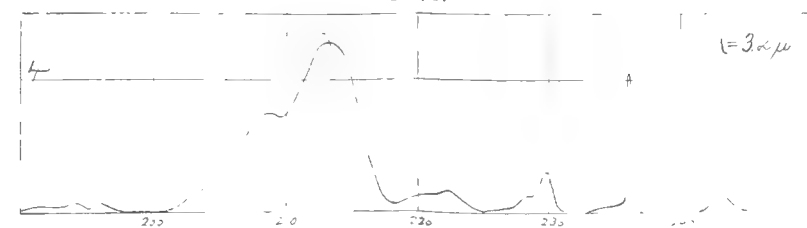


FIG. 9.

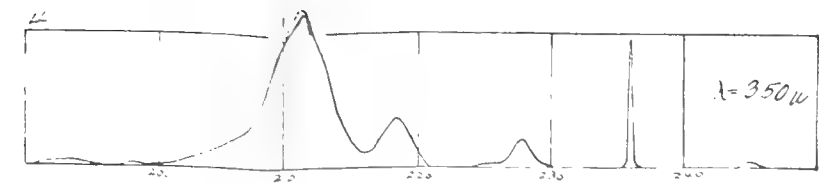


FIG. 10.

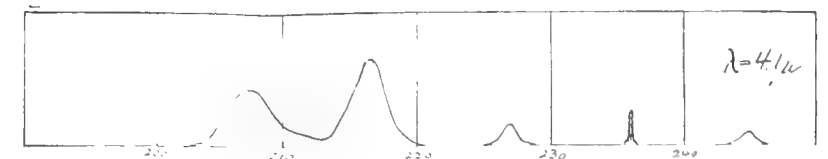


FIG. 11.



FIG. 12.

**WOOD GRATING No. 7.**

GRATING SPACE: .00123 cm.

ANGLE BETWEEN COLLIMATORS: 19° 2.

Form of Groove as in Fig. 4 (Text).

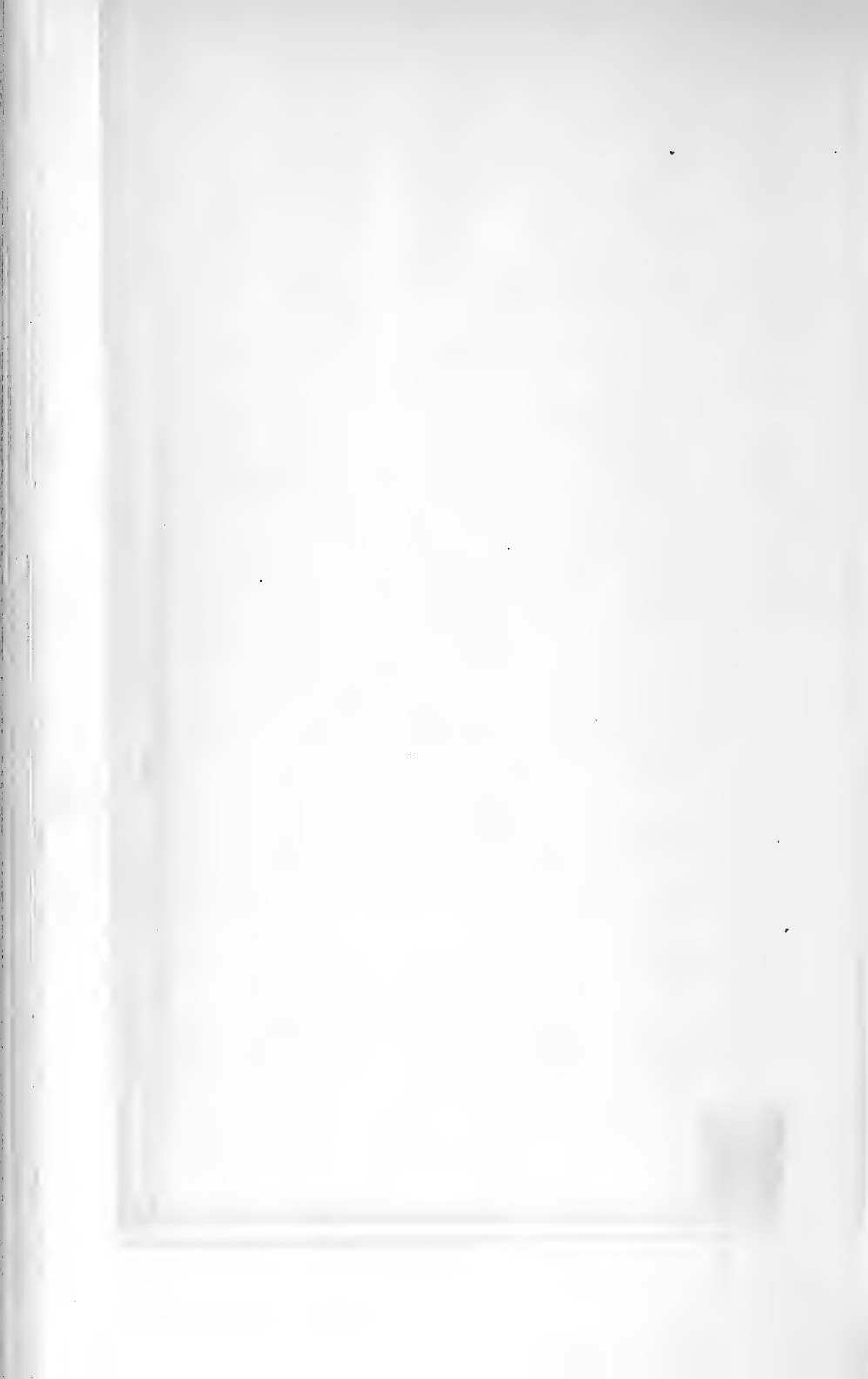


FIG. 13.

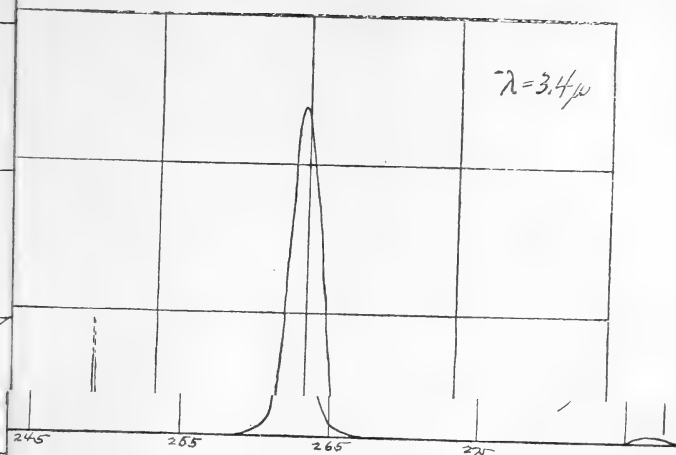
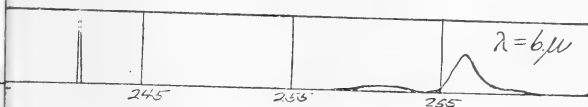


FIG. 20.



**GRATING No. 10.**

GRATING SPACE: 0.00067 cm.

ANGLE BETWEEN COLLIMATORS:  $2\theta = 30^\circ$ .

of Groove (Approximate).

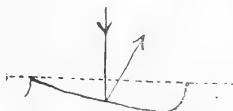






FIG. 1.

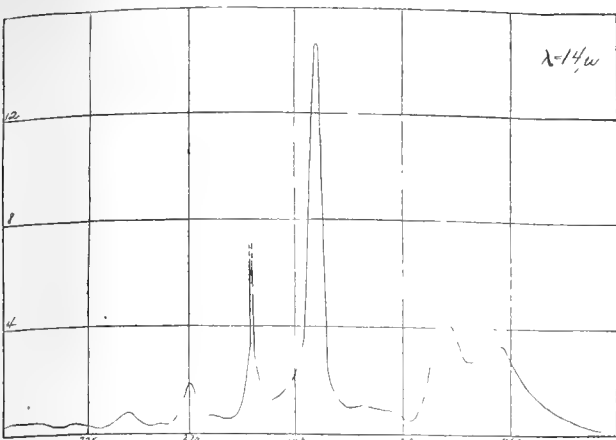


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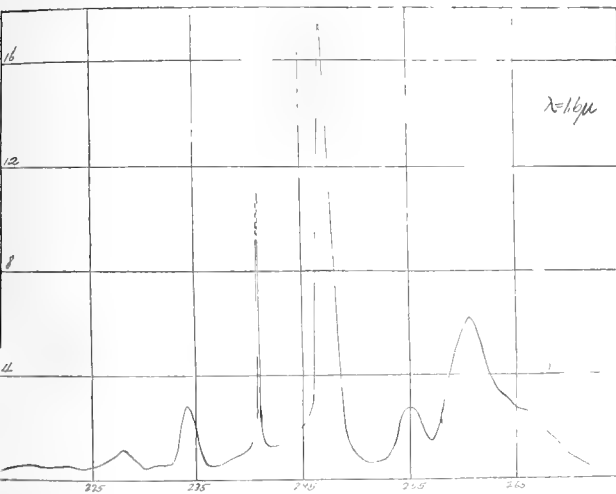


FIG. 3.

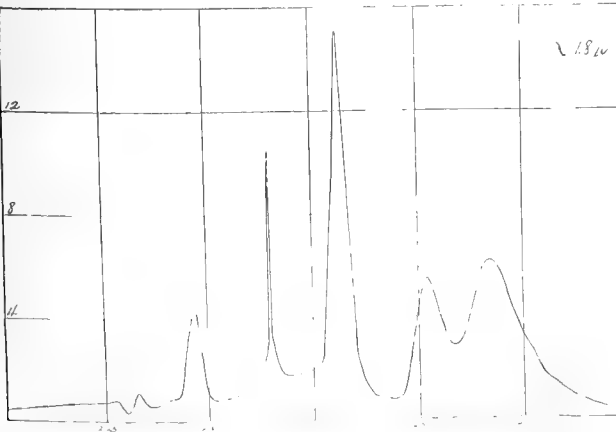


FIG. 4.

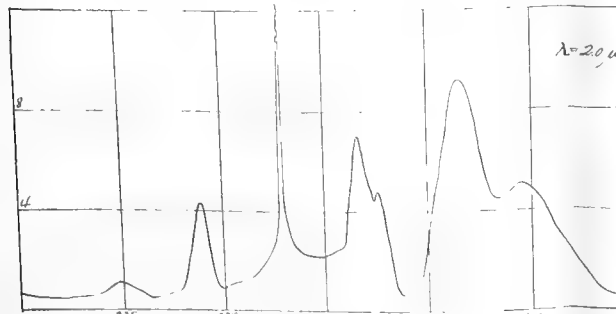


FIG. 5.

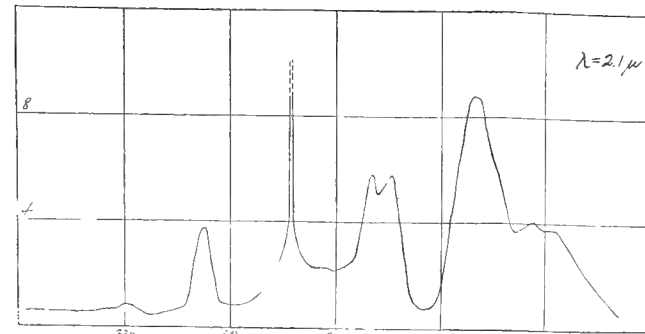


FIG. 6.

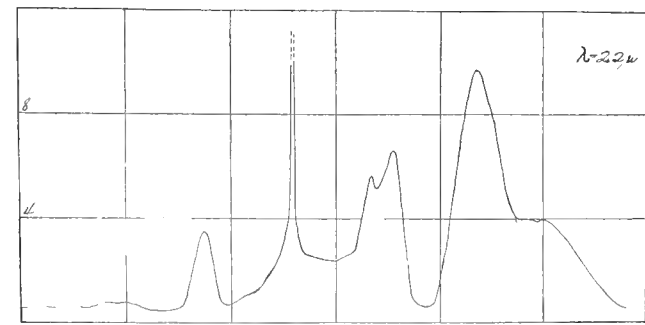


FIG. 7.

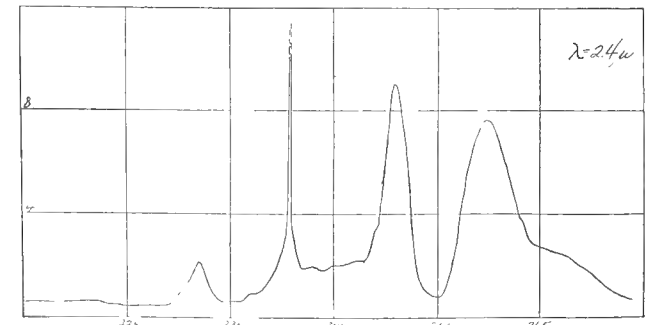


FIG. 8.



FIG. 9.

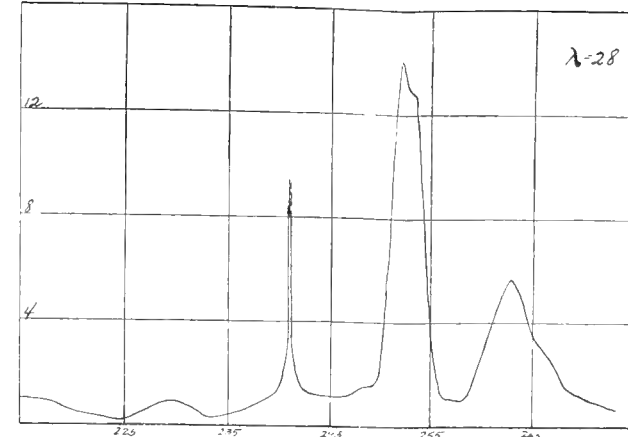


FIG. 10.

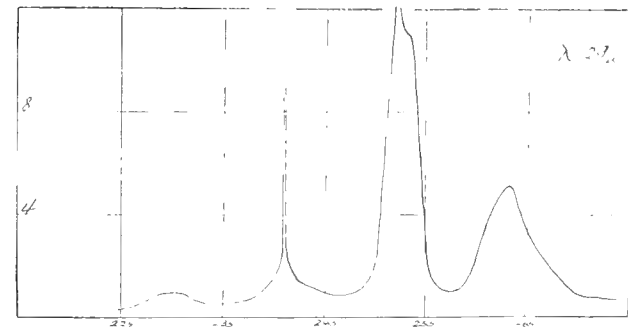


FIG. 11.

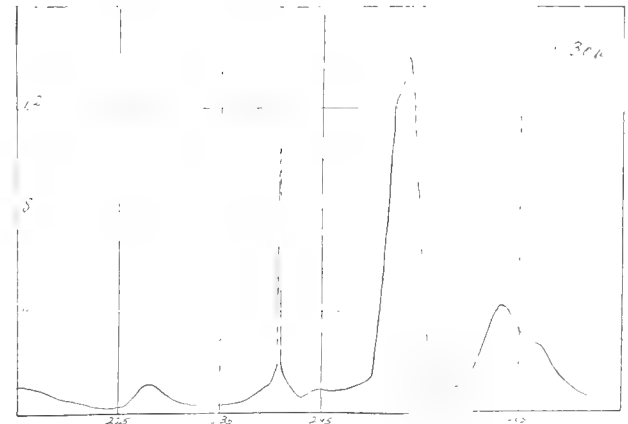


FIG. 12.

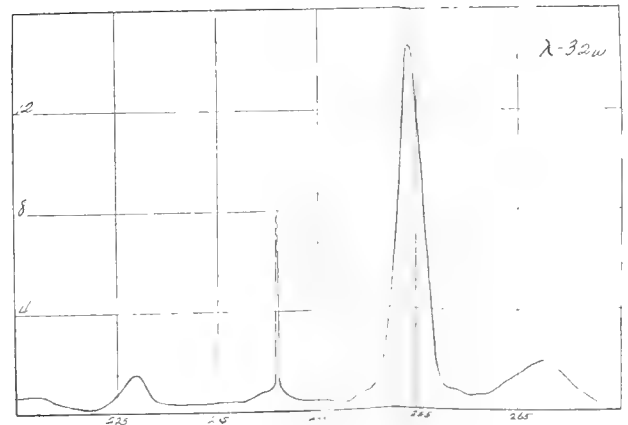


FIG. 13.

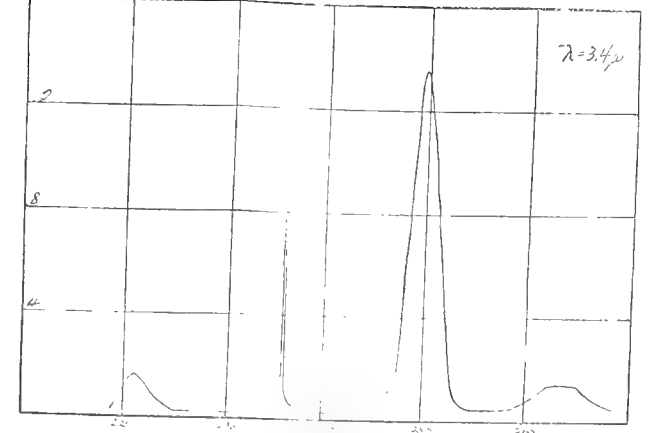


FIG. 14.

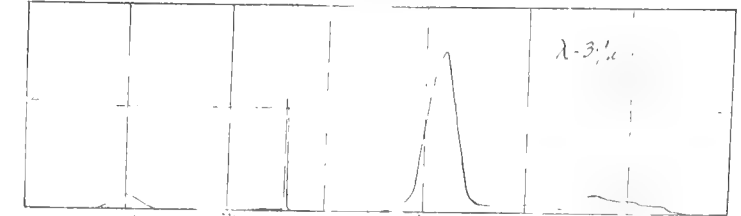


FIG. 15.

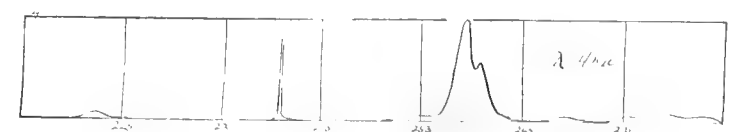


FIG. 16.

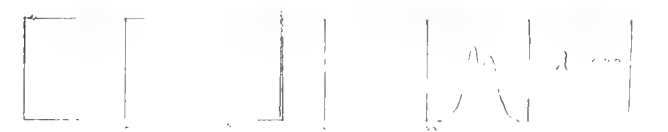


FIG. 17.

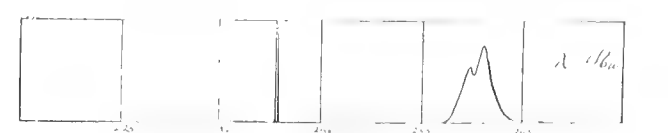


FIG. 18.

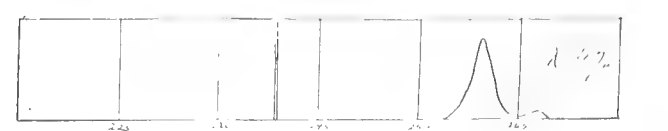


FIG. 19.

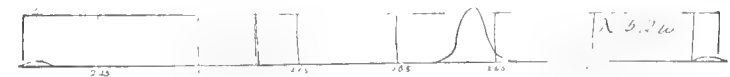


FIG. 20.

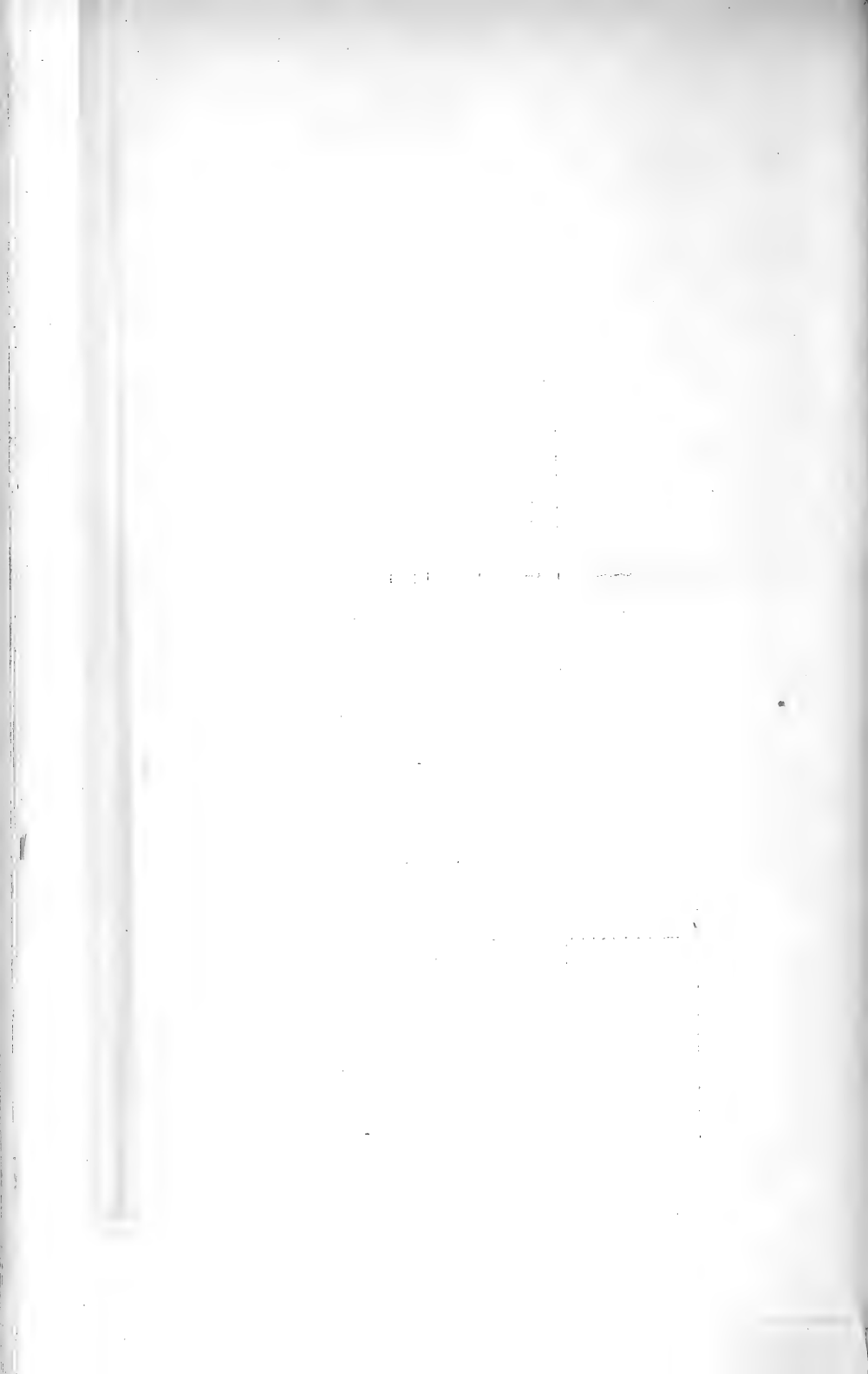
**BRACKET GRATING No. 10.**

GRATING SPACE: 0.0067 cm.

ANGLE BETWEEN COLLIMATORS:  $2\theta = 30^\circ$ .

Form of Groove (Approximate).









THE  
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AND  
JOURNAL OF SCIENCE.

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[SIXTH SERIES.]

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NOVEMBER 1911.

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LXVI. *The Positive Ionization from Hot Salts.* By O. W. RICHARDSON, *Professor of Physics, Princeton University*.\*

IN two papers published in the *Philosophical Magazine* for December 1910 the author described experiments which were made in order to determine the value of the specific charge ( $e/m$ ) of the positive thermions emitted by the salts of the alkali metals. The results of the experiments showed that the positive ions, in each case, were atoms of the basic metal carrying a single electronic charge. Since then the investigation has been extended in different directions.

*The Specific Charge of the Ions.*

In the first place the value of  $e/m$  has been measured for the salts of a number of other elements. At the end of the second of the papers referred to, it was pointed out that one very interesting question which arises is whether the salts of polyvalent elements will emit ions carrying multiple electronic charges. The early work of Beattie† showed that compounds of zinc were very efficient in producing positive ionization, whilst the work of Arrhenius, H. A. Wilson, and others on the conductivity of flames and salt vapours had shown that similar properties were to be expected of the salts of the alkaline earth metals. Attention was therefore directed to the salts of the zinc and calcium groups of metals. All these metals

\* Communicated by the Author.

† *Phil. Mag.* [5] vol. xlviii. p. 97 (1899).

are divalent. The results of the measurements of  $e/m$  will now be described briefly for each of the salts examined. The method was the same as that described in previous papers.

*Beryllium Nitrate.*—The salt used was supplied by Kahlbaum, Berlin. For the freshly heated salt the following values were obtained :— $e/m=360$ , and  $m/H=27$ .  $m/H$  is the mass of the ions which carries the same charge as a hydrogen atom in electrolysis. Additional measurements were made after 16, 23, and 39 hours' heating respectively. They all gave identical values, viz.,  $e/m=325$ , and  $m/H=29.5$ . The ionization became too small to measure after this continued heating, and in raising the temperature the strip of platinum melted.

The values of  $m/H$  for the ions  $\text{Be}_+^*$  and  $\text{Be}_{++}$  would be 9.1 and 4.55 respectively. There is thus no evidence of the emission of these ions from beryllium oxide (into which beryllium nitrate is converted when heated). This was rather to be expected, since in the case of the salts of the alkali metals efficiency of thermionic emission diminishes rapidly with diminishing atomic weight, and the salts of the beryllium group are far less efficient than those of alkali metals of neighbouring atomic weight.

It is probable that the ionization observed with this substance is due to contamination with alkaline impurities (salts of sodium and potassium). It is to be remembered that the thermionic test for these substances is extraordinarily delicate, so that even what are ordinarily known as chemically pure substances may be expected to be quite impure when tested in this way. Quantities of the salts of the alkali metals which would be incapable of detection by the most delicate balance are capable of giving rise to a large thermionic current for a very long time. Mr. C. J. Davisson, working in this laboratory, has recently examined a specimen of beryllium sulphate which was supplied to him by Mr. Parsons, who is one of the leading authorities on the compounds of this element. According to Mr. Parsons the specimen in question is in all probability the purest specimen of a beryllium salt which has ever been prepared. Although Mr. Davisson examined the thermionic emission of this substance most carefully, all the ions which it gave off had a value of  $e/m$  exceedingly close to that given by salts of potassium, with which it must have been contaminated.

More convincing reasons will be given later for believing

\* Throughout this paper a positive ion with a single electronic charge will be denoted by  $\text{M}_+^*$ , and one with a double charge by  $\text{M}_{++}$ , where M is the chemical symbol for the atom of the element.

that the thermions, which give values of  $m/H$  between 25 and 35 or thereabouts, in cases where the chemical composition does not make such values probable *a priori*, arise from contaminations with the salts of the alkali metals. The view has been recently advocated by several authors that these ions are charged atoms or molecules of some gas, such as carbon monoxide, which has access to the heated salt. I believe this view to be a mistaken one.

*Magnesium Chloride.*—The curves given by this substance were irregular, and made the experiments somewhat unsatisfactory. There is a great deal of difference between the salts of the same metal in this respect. I am inclined to attribute the irregularity to the salt redistributing itself on the strip during the course of an experiment; some salts seem to have a tendency to collect into irregular lumps, whilst others form a nice uniform layer all over the strip.

The ionization from magnesium chloride was relatively small. The only satisfactory experiment gave the values  $e/m=360$ , and  $m/H=27$ . This may have been either  $Mg^+$  or  $Na^+$ , but there was certainly no indication of  $Mg^{++}$ . The magnesium chloride used was Kahlbaum's "Zur Analyse."

*Zinc Chloride.*—The curves given by this salt were also somewhat irregular. The ionization developed at a low temperature and did not persist very long. The two most satisfactory determinations gave the values  $m/H=78$ , and  $m/H=44$  respectively. The mean of these is 61 as against 65 for  $Zn^+$ . The zinc chloride used was Kahlbaum's granulated.

*Zinc Bromide.*—After some preliminary experiments, which gave rather irregular curves, some very satisfactory results were obtained with this substance. The deflected curves were similar and symmetrical, and the undeflected curve ( $H=0$ ) was similar and exactly halfway between them. The mean of two concordant experiments gave  $e/m=194$ , and  $m/H=49.4$ . This is almost halfway between the values of  $m/H$  for  $Zn^+$  and  $Zn^{++}$ , which are 65 and 32.5 respectively. It may imply a mixture of these ions, or it may be due to  $Zn^+$  contaminated with alkalis.

*Zinc Iodide.*—This substance behaved rather like zinc bromide. The freshly heated substance gave irregular curves which afterwards became more consistent. Two concordant sets of curves, which were symmetrical about the undeflected position, gave for the mean values  $e/m=234$  and  $m/H=41.4$ . These are much nearer the values for  $Zn^{++}$  than for  $Zn^+$ .

Considering the results for the zinc haloid compounds

together the average values of  $m/H$  for the positive ions they emit are:—for  $\text{ZnCl}_2$  61 ; for  $\text{ZnBr}_2$  50 ; and for  $\text{ZnI}_2$  42. There is thus an apparent decrease in the mass of these ions with increasing atomic weight of the haloid constituent. In the case of zinc chloride it is clear that the bulk of the ions are  $\text{Zn}_+$ . In the other cases they are probably a mixture of  $\text{Zn}_+$  and  $\text{Zn}_{++}$ , but I do not think that this view can be regarded as certain until it can be demonstrated that part of the ionization in the case of the bromide and iodide was not due to alkaline impurities. The breadth of the curves for a given applied potential difference was least for the chloride, and greatest for the iodide, indicating a gradually diminishing degree of purity in the ionization. I was not, however, able to resolve the curves so as to obtain more than one hump with the appliances then available, although the matter will be investigated more fully later.

The zinc bromide and iodide were supplied by Messrs. Eimer and Amend, with no indication as to their purity beyond the usual guarantee under the Food and Drugs Act.

*Calcium Nitrate.*—When calcium nitrate is heated it is converted into the oxide, and, as is well known, this endows the platinum on which it is placed with the power of emitting large numbers of negative electrons. When the nitrate was first heated a large positive ionization was obtained, apparently during the conversion of the nitrate into the oxide. The emission then stopped rather abruptly, and further heating of the oxide did not improve matters. On adding more nitrate to the lime and reheating very good curves were obtained. These gave the values:— $e/m=222$  and  $m/H=43.5$ . This value of  $m/H$  is sufficiently close to either  $\text{Ca}_+$  ( $=40$ ) and  $\text{K}_+$  ( $=39$ ), but the comparatively abrupt stoppage of the positive emission when the oxide state is reached is against the impurity explanation in this case. The experiments showed quite clearly that there was no appreciable quantity of  $\text{Ca}_{++}$ . The experiments just described have demonstrated the existence of the ion  $\text{Zn}_+$ , the probable existence of  $\text{Ca}_+$  and of  $\text{Zn}_{++}$ , and the possible existence of  $\text{Mg}_+$ . It was clear that more light would be thrown on these phenomena by the investigation of compounds of some of the heavier atoms, such as barium for example, where the possible ions,  $\text{Ba}_+$  and  $\text{Ba}_{++}$ , would be readily distinguishable from ions such as  $\text{K}_+$  and  $\text{Na}_+$  which arise from traces of the salts of the alkali metals which are always liable to be present.

This part of the investigation has been continued from this



stage by Mr. C. J. Davisson\*, who has made several important improvements in the apparatus which I had used, and has made a very thorough examination of the emission from the salts of the alkaline earth metals. He finds that all the ions emitted by these salts fall into two groups: (1) those which have values of  $e/m$  corresponding to an atom of the earth metal which has lost a single electron, and (2) those which have values in the neighbourhood of those corresponding to  $K_+$  and  $Na_+$ , or intermediate between them. In point of fact nearly all the ions of the second group were quite close to the value corresponding to  $K_+$ . The experiments with barium salts were particularly instructive. With a single exception all the salts tried furnished only ions of the type  $Ba_+$ . No evidence could be obtained for the emission of ions of the type  $Ba_{++}$ ,  $Sr_{++}$ ,  $Ca_{++}$ , and  $Mg_{++}$  from any of the salts, although they were looked for most carefully by Mr. Davisson.

The discovery by Garrett† that the pressure of the surrounding gas had an important effect on the emission of positive ions from hot aluminium phosphate seemed to render it probable that at pressures high enough to cause a considerable increase in the thermionic current, part at any rate of the positive ions might be expected to be charged atoms or molecules of the surrounding gas rather than atoms of the basic metal. It seemed that this question could be definitely settled by making measurements of  $e/m$  for the ions from such salts in gases at low pressures. According to the curves given by Garrett the ionization from aluminium phosphate is very much greater at a pressure of one-twentieth of a millimetre of air or carbon dioxide than it is in a good vacuum. Strictly speaking the method of measuring  $e/m$  assumes that the number of ions which undergo collisions between the electrodes should be negligible, but it seemed likely that the method would give fairly satisfactory results up to pressures of this order. I therefore suggested to Mr. Davisson that he should make measurements of the value of  $e/m$  for the positive ions emitted by aluminium phosphate in different gases at different pressures‡. He found that in air and hydrogen the value of  $e/m$  was practically the same at all pressures below about one-tenth of a millimetre, and was identical with the value in carbon dioxide at pressures less than about one-thirtieth of a millimetre. The value of  $e/m$  which he found corresponded very closely with that for

\* Phys. Rev. vol. xxxii. p. 620 (1911).

† Phil. Mag. [6] vol. xx. p. 573 (1910).

‡ C. J. Davisson, Phys. Rev. vol. xxxii. p. 620 (1911).

$\text{Na}_+$ , indicating that the large ionization usually observed with this substance is due to contamination with the salts of the alkali metals. A specimen of calcium sulphate, which he examined in a similar way, gave values of  $e/m$  corresponding to  $\text{Ca}_+$  in air at all pressures below about 0.1 millimetre. The changes in the apparent value of  $e/m$  which occurred at still higher pressures were such as would be expected to arise from the interference of the gas molecules with the free motion of the ions, and they do not indicate any change in the nature of the ions themselves, at low pressures, as the pressure of the gas is altered. This is true for such very different gases as hydrogen, air, and carbon dioxide. A full account of Mr. Davisson's work will be published shortly, but it may be permissible to state that he has devised a number of other experiments which fully confirm the results of those which have been described. The evidence in fact leaves no doubt that only a negligible fraction, if any, of the positive thermionic current from salts is carried by ions which are not metallic atoms.

I am aware that this is a standpoint which is diametrically opposed to the views which have been expressed by a number of recent investigators of the subject\*. The direct evidence to the contrary is, however, quite meagre. Horton† has already pointed out that the hypothesis of neutral doublets put forward by Garrett‡ fails to account for one of the most prominent figures of the case, which is, that these substances emit a large positive ionization when the negative emission is too small to measure. Garrett has also adduced direct evidence that a considerable part of the emission from aluminium phosphate is carried by hydrogen atoms. Davisson has looked for this phenomenon, using a method which I believe to be more reliable, and has been unable to confirm it.

Apart from the evidence brought forward by Garrett to support his hypothesis of doublets and his experiment on the magnetic deflexion of the positive ions, the remaining evidence as to their nature is of an indirect character. The bulk of it relies on the effect of various agents, chiefly gaseous, in increasing the quantity of the emission. In the light of experiments which will be described below, it would seem to require great boldness to draw any conclusions as to the

\* Cf. Garrett, *Phil. Mag.* [6] vol. xx. p. 573 (1910). Horton, *Camb. Phil. Proc.* vol. xvi. p. 89 (1910); *Proc. Roy. Soc. A.* vol. lxxxiv. p. 433 (1910). W. Wilson, *Phil. Mag.* [6] vol. xxi. p. 634 (1911).

† *Camb. Phil. Proc.* vol. xvi. p. 89 (1910).

‡ *Loc. cit.*

nature of the ions from evidence of this sort. Horton's\* experiment showing that carbon monoxide is evolved when aluminium phosphate is heated is not of this character, but it does not seem to be to the point. Apart from the objection that practically everything gives off small quantities of carbon monoxide when heated, there is no evidence that there is any connexion between the emission of this gas and that of the positive ions. On my view of course the material nature of the ions would not be discovered by a spectroscopic examination of the gas evolved as they would collect on the negative electrode and stay there.

*Ionization from Salts in a Gaseous Atmosphere.*

A large number of experiments have been made with the object of measuring the magnitude of the positive emission from salts under different conditions. The apparatus first used was similar in principle to the arrangements employed by Garrett in his experiments on aluminium phosphate, and by Horton in his experiments on sodium phosphate. A horizontal platinum strip was heated by an electric current, and the central portion was covered with a thin layer of the salt under examination. The temperature of the central part of the strip was obtained by a modification of Kelvin's double-bridge method of measuring small resistances, the connexions to the strip being made by means of platinum wires welded on to it, at a distance from each end of the strip equal to about a quarter of the whole length. All the strips used were cut on the dividing-engine, and their edges were exactly parallel and 2 mm. apart. The area covered by the heated salt was always about 0.2 sq. cm., and the area of hot platinum which was not so covered, including the back of the strip, was always about 0.6 sq. cm. The salt occupied the middle centimetre of the upper surface of the strip.

In this investigation all the currents were measured by means of a Dolezalek electrometer which gave a deflexion of 800 mm. per volt. For currents less than  $10^{-8}$  amp. the time-rate of deflexion was used, a one-microfarad subdivided standard condenser being connected with the insulated quadrants. For larger currents the electrometer was shunted with a resistance of 1 megohm or any fraction thereof, and the steady deflexions observed. This arrangement is very convenient, since, by merely changing a few keys, any

\* Proc. Roy. Soc. A. vol. lxxxiv. p. 433 (1910).

current between  $10^{-13}$  ampere and 1 ampere can be readily measured by the same instrument.

The temperatures were obtained by measuring the resistance of the strip at the temperature of the room and at the melting-point of sodium sulphate, of potassium sulphate, and of platinum, and constructing a calibration curve from the data thus obtained.

A number of experiments were first made with tribasic sodium phosphate ( $\text{Na}_3\text{PO}_4$ , c.p., by Eimer and Amend). The results were similar to those obtained by Horton with sodium phosphate. In air there was a maximum positive emission at 2.3 millimetres pressure when the temperature was  $730^\circ\text{C}$ . At very low pressures the emission was quite small, being only one-fiftieth of the maximum at 0.00002 mm. pressure. The value of the maximum current at this temperature was  $3.3 \times 10^{-9}$  amp.

A more detailed examination was made in the case of sodium sulphate ( $\text{Na}_2\text{SO}_4$ , by Kahlbaum). The salt was placed on the strip and melted in the air of the room before being tested. It emitted white fumes during the process. The general character of the thermionic behaviour of this substance was found to be similar to that of the sodium phosphate. When the salt was heated at a constant temperature the emission increased rapidly during the first five minutes and then fell in the manner which is characteristic of the positive ionization from hot bodies generally. The following observations, taken at  $1005^\circ\text{C}$ ., are typical:—

Time heated, minutes .....	2	5	6	9	14	20	32	60	150
Thermionic Current..... ( $1=1.25 \times 10^{-7}$ amp.)	6.0	25	26	23	22	15	13	9.5	4.6
Time heated .....	190	215	242	295	330	990	1140	1290	
Current .....	3.3	0.86	0.26	0.17	0.12	0.025	0.020	0.0167	

After about 24 hours' heating at this temperature the rate of decay of the emission becomes quite small, and might be due to loss of salt by evaporation. In these experiments sudden but rather temporary increases of the emission are apt to occur, particularly during the period between the lapse of half an hour and an hour and a half from commencing to heat the salt. Such increases have been omitted from the table as far as possible.

As a preliminary to further experiments all the specimens

of salt tested were positively charged and heated for 24 hours or more in a good vacuum until they got into a fairly steady state. Measurements of the positive emission were then made with both increasing and diminishing pressures of air up to about 10 mm. The results do not seem to be absolutely definite, as the curves connecting the ionization and the pressure often differed considerably under what were apparently the same conditions. The salt behaved as though its nature was changing considerably during the course of the experiments. The rough outlines of the phenomena were, however, definite enough. The ionization was always small at a very low pressure, and increased rapidly with the pressure at low pressures. In many cases a maximum value of the emission was observed at a certain pressure, although this did not always happen. When there was a pressure of maximum emission it always occurred at a higher pressure the lower the temperature. This point is illustrated by the following table, which shows (column 2) the pressure at which the emission was a maximum at a series of temperatures (column 1), the value of the maximum positive emission (column 3), and the value (column 4) of the small emission given at the lowest pressure (column 5) which could be attained by working the Gaede pump continuously:

Temperature.	Pressure for maximum emission.	Maximum Emission.	Least Emission.	Least Pressure.
730° C.	20 mm.	$1.67 \times 10^{-11}$ amp.	$8 \times 10^{-13}$ amp.	0.00003 mm.
1005° C.	4 mm.	$3.5 \times 10^{-8}$ amp.	$2 \times 10^{-9}$ amp.	0.0003 mm.
1160° C.	0.2 mm.	$7.8 \times 10^{-7}$ amp.	$1.3 \times 10^{-7}$ amp.	0.0003 mm.

A similar displacement of the maximum emission towards higher pressures at lower temperatures was found by Garrett to be exhibited by aluminium phosphate.

This maximum emission at a certain pressure does not appear to occur at a low temperature with a specimen of the salt which has been heated for a long time at a high temperature. A specimen which had been heated for considerable periods at temperatures as high as  $1160^{\circ}\text{C.}$  gave the following values of the thermionic current at a series of pressures at  $730^{\circ}\text{C.}$ :

Pressure (mm.) ...	·25	·45	1·3	1·73	2·2	1·2	·75	·45	·26	·14	·012
Current .....	25	38	42	41	42	46	48	47	40	20	17
(1=4×10 <sup>-12</sup> amp.)											

The order from left to right is the order of the observations in time. The slightly higher values with diminishing than with increasing pressures is a spurious effect, caused by the temperature having undergone a slight increase temporarily while the pressure was being reduced. Subsequent experiments, made at a higher temperature ( $1160^{\circ}\text{C.}$ ), in such a way that the temperature was kept constant by a continuous regulation of the controlling resistances, as the pressure was altered, showed that there was a slight difference in the position of the ascending and descending curves, but in the other direction. The curve for ascending pressure indicated rather bigger values of the emission at a given pressure than the descending curve. This experiment was carried out with a specimen of the salt which had been heated for a long time. Continued heating only seems to remove the pressure of maximum emission when the test is made at a low temperature. A specimen which had been heated continuously in a vacuum for four days still gave a quite definite maximum in the neighbourhood of  $0.16\text{ mm.}$  both on the ascending and descending pressure curves at  $1160^{\circ}\text{C.}$  The maximum pressure was somewhat higher for the ascending than for the descending curve; in all probability this only means that the true equilibrium was not completely reached when the observations were taken.

The maximum in the pressure curves does not appear to be due to lack of saturation of the thermionic current. I have examined this point most carefully by taking a separate current-E.M.F. curve for each point on the pressure-current curve. It occurs with voltages which are too small for ionization by collisions to be a factor, and, in addition, the shift of the maximum with temperature is against this explanation.

The following numbers are typical of the results obtained with a specimen of sodium sulphate at  $1160^{\circ}\text{C.}$  which has been heated for a long time at that temperature:

Pressure increasing.

Pressure (mm.) ...	·01	·084	·13	·18	·26	·31	·46	1.16	1.84
Current .....	67	71	77	82	84	85	76	71	47
(1 = $1.25 \times 10^{-8}$ amp.)									

In this experiment the heating current was continuously regulated so that practically no fluctuation occurred in the temperature whilst the pressure was being varied.

*Experiments with water vapour.*—Immediately after the

experiment which gave rise to the preceding numbers, the effect of water vapour on the emission was tried. Successive increments in the pressure were obtained by connecting to a small side chamber, which was exhausted except for the fact that there was a small quantity of water in the bottom of it. The approximate values of the pressures after the addition of water vapour were obtained from the depression of a barometer column. The values of the thermionic current with increasing pressure were as follows:—

Pressure (mm.) ...	·01	6·5	11	14	16	18	21	22
Current .....	86	203	144	118	102	93	84	76

( $1=1\cdot25\times10^{-8}$  amp.)

The first reading at 0·01 mm. corresponds to the air initially present in the apparatus. On pumping out the water vapour the following values of the emission were obtained at the pressures stated:—

Pressure (mms.) ...	22	10	6·5	5	4	3	2	1·5	·5	·33
Current.....	75	130	174	250	260	306	340	456	550	520

( $1=1\cdot25\times10^{-8}$  amp.)

---

Pressure (mms.) ...	·15	·030	·005
Current.....	490	410	220

( $1=1\cdot25\times10^{-8}$  amp.)

The maximum emission in water vapour is thus about five times as great as in air at this temperature. The pressure of maximum emission also appears to be somewhat higher (about ·5 mm. as against ·2 mm.).

This treatment with water vapour apparently produced a permanent change in the salt, as the maximum emission in air when measured at the same temperature was found to be only  $1\cdot2\times10^{-7}$  amp. as against  $1\cdot2\times10^{-6}$  amp. previously.

The mode of variation with the pressure at very low pressures has been examined very carefully, as it seemed that this would be likely to throw some light on the nature of these rather involved phenomena. The only conclusion that I have been able to come to is that at very low pressures the emission is a linear function of the pressure. This is a state of things that would occur on almost any view of what is going on. At very low pressures the phenomena seem very variable; sometimes a change of pressure from about ·00005 to ·01 mm. would increase the emission by a factor of eight, whilst at others it would scarcely affect it. I have

been quite unable to locate the determining cause of this difference under conditions which were apparently identical.

When the salt was heated to a higher temperature than that at which observations were taken, it was always found that the emission was greater than would otherwise have been the case. This effect, which persists for some time, has been observed, by Horton, to occur when sodium phosphate is heated.

No negative emission, comparable in amount with the positive, was observed during these experiments with sodium sulphate, though it was frequently looked for when the conditions seemed favourable.

#### *Experiments with a Platinum Tube.*

A general survey of the experiments on sodium sulphate which have just been described, together with the rather similar results obtained by previous observers working with a similar type of apparatus on aluminium phosphate and sodium phosphate, did not seem to point to any very definite conclusion as to the nature of the action by which the pressure of the gas gives rise to such great variations in the amount of the positive emission. It seemed likely that more light might be thrown on these phenomena if the measurements were made under conditions differing as widely as possible from those which had held previously. With this object in view a new apparatus was constructed. The salt (about one gram as a rule) was placed in the bottom of a platinum tube which was closed at one end. The closed end was tapered somewhat and the dimensions of the tube, neglecting the taper, were:—length 25 cm., outside diameter 2 cm., and wall thickness .02 cm. In the early experiments this tube was heated directly in a Heraeus platinum resistance furnace, but it was found to collapse under the heat. It was therefore placed, after trying several other materials, in a mild steel tube which served as a crucible. The steel tube was drilled out of  $1\frac{3}{8}$  inch mild rod, so that the platinum tube went into it with a loose sliding fit. About  $1\frac{1}{2}$  inches of the crucible was left solid at the bottom, and a hole about  $1\frac{1}{2}$  an inch deep was drilled to receive the end of a platinum-platinum-rhodium thermo-couple. This was standardized against a platinum resistance thermometer obtained from the Cambridge Scientific Instrument Co., and known to be right. The Heraeus tubular furnace was placed vertically, the crucible and connexions being at the top, and the thermo-couple coming out at the bottom. The ends were closed with sheet asbestos, and the space between the porcelain



tube of the furnace and the crucible was packed with kieselguhr. It was thought that this arrangement would protect the iron from the action of the air. The projecting end of the crucible was kept cold by means of a water jacket, so as to admit of the central electrode being cemented in with sealing-wax. The central electrode itself was a brass tube 1 cm. outside diameter, closed and tapered at the lower end, and was brazed into a wider tube a little narrower than the steel crucible. The electrode was insulated from the crucible by means of a glass bush in the sealing-wax joint. It was cooled by a blast of air blown down the inside of it through an axial glass tube, and also by a forced draught driven against brass flanges soldered to the upper projecting parts outside. Water cooling could not be used conveniently as it was necessary to insulate the inner electrode from the crucible. With this arrangement the central electrode was always axial to the platinum tube, and, in sealing it in, matters were arranged so that the end of the brass tube was about 6 mm. above the surface of the salt. A side tube leading from the wide part of the inner electrode enabled the crucible and contents to be connected to a Gaede pump and exhausted.

At room temperatures the apparatus was perfectly air-tight, but at high temperatures a little gas leaked through the hot steel. At  $980^{\circ}\text{C}$ . it was not possible to pump down to less than  $\cdot 006$  mm. If the gas thus evolved came from the air outside it would presumably be a mixture of carbon monoxide and nitrogen, since the oxygen of the air would combine with the carbon of the steel during the transference. This leakage was much less at lower temperatures, and it seems highly probable, as most of the experiments were carried out at temperatures under  $800^{\circ}\text{C}$ ., that most of the gas which appeared to leak in was evolved by the heated salts.

Some experiments were also made with a *hot* platinum electrode insulated on quartz. These were not carried very far as it was found that salt was deposited on the inner electrode, and that there was always a leak both ways which increased rapidly with increasing potential difference. The results of these experiments are difficult to explain, except on the view that when the hot salt is bombarded by positive ions the emission is increased, even when the applied potential difference is considerably less than that required for the positive ions to produce fresh ions by collisions in the ordinary way.

Preliminary experiments were first made without any salt

in the platinum tube. Before each experiment the tube was cleaned by boiling in hydrofluoric acid, nitric acid, and distilled water in succession. Similar treatment was also accorded to the platinum strips which were used in the other type of experiment. Current-E.M.F. curves taken at a temperature of about  $940^{\circ}\text{C}$ . and a series of different pressures gave the numbers in the following table:—

Volts .....	40	80	120	160	200	240	280	320	360
Pressure= $\cdot 0075$ mm. ....	1	1.23	1.45	1.57	1.68	1.77	1.90	2.13	2.31
do. =about $\cdot 5$ mm. ...	1	1.25	1.44	1.54	1.61	1.90	2.45	3.47	5
do. = $5\cdot 5$ mm. ....	1	1.29	1.53	1.71	1.80	1.83	1.83	2.5	15

The three lower rows give the thermionic currents (positive emission) at the respective pressures when the voltage applied is that at the top of each column. The unit of current is about  $10^{-7}$  amp. Saturation was never reached, strictly speaking, in these experiments, as the current always increases slowly with increasing voltage. The mode of variation does not differ much at different pressures for voltages under 200, so that it seemed reasonable to suppose that a comparison of the thermionic currents at a constant voltage in the range between 40 volts and 200 volts would be a fair way of testing the thermionic emission at different pressures. In each test of the pressure variation, experiments were made both with 40 and also with 160 volts applied potential difference, in order to make sure that the applied voltage was not an important factor in the results. With the empty platinum tube the pressure of the air had very little effect on the positive emission, either with 40 or 160 volts applied potential difference. A specific test at  $945^{\circ}\text{C}$ . with 160 volts gave a current of 21.7 divisions (1 div. =  $1\cdot 25 \times 10^{-8}$  amp.) at 0.01 mm. pressure, and 21.8 divisions at 12.0 mm. pressure. The results obtained with the lower voltage and with changes to intermediate pressures were similar, except that slightly larger increases were usually observed. The increases might always have been accounted for as experimental errors, but it is significant that out of 6 sets of observations every one showed a slight increase with increased pressure. This result is consistent with the author's earlier experiments\* on the ionization from pure platinum in air, according to which the effect of the air on the pure platinum itself should have called for a current of one-half to one division in the case of these observations. It is clear that in these experiments the emission from the empty platinum tube was greater than that which would have arisen from pure platinum at the

\* Phil. Trans. A. vol. ccvii. p. 40 (1906).

same temperature, but no systematic attempt was made to reduce it, as it was quite small compared with the effects produced by all the salts investigated, with one exception.

The experiments with the different salts will now be considered in the order in which they were carried out. In every case current-E.M.F. curves were taken at three different pressures: (1) at the lowest pressure attainable by working the Gaede pump continuously, usually about 0.004 mm., (2) at a pressure between 0.5 and 0.8 mm., and (3) at a pressure between 5 and 10 mm. This was done before the experiments on the variation with air pressure were carried out, in order to make sure that there was nothing exceptional about the relation between the current and the voltage. The dependence upon pressure was examined under constant potentials of 40 and 160 volts respectively, and in each case with both rising and falling pressures. As a rule a series started with the highest attainable vacuum, so that the first observations were with increasing pressures.

*Sodium Sulphate.*—The current-E.M.F. curves were so similar to those with the empty tube as to call for no special description. In this case the current-pressure curves were taken by starting from the highest pressures. The steady values with +40 volts applied P.D. are given in the following table in the order in which they were taken.

Pressure (mm.) .....	8.9	3.3	1.1	.38	.14	.033	.006	.0048
Current .....	42	39	33	26.8	25	24	24	24*
								27
(1 = $1.25 \times 10^{-8}$ amp.)								
Actual Temperature, degrees centigrade.	797	...	...	...	...	...	795	

Pressure .....	.004	.037	.064	1.2	.50	.93	1.6	7.6
Current .....	28	23.5	29	30	36.5	44	52	56
Actual temperature...	797	...	...	...	...	...	799	

The general course of the readings with +160 volts was quite similar, namely,

Pressure.....	7.8	6.1	4.25	3.15	2.2	1.36	.90	.40	.10	.006
Current .....	36.9	35.2	32.2	28.2	24.4	20.3	17.2	13.7	13.2	12.0
Actual temperature ...	783	...	...	779	...	...	...	...	...	774

Pressure...	.005	.033	.22	.68	1.1	1.6	2.5	3.3	5.2	6.5	8.1
Current ...	11.6	11.5	11.3	13.1	14.6	15.6	16.7	15.6	15.5	15.1	14.5
Actual temperature	767	...	...	734	...	...	...	728	...	...	720

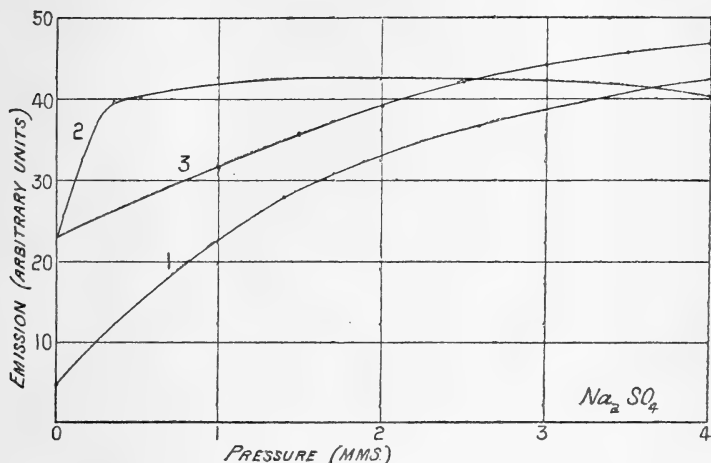
\* Reading rose slowly from 24 to 27.

These results are particularly instructive. In the experiments with +40 volts the temperature was very constant, the extreme variation being  $4^{\circ}\text{C}$ . There is, nevertheless, a considerable difference between the emission at a given pressure on the outward and return journeys. This is owing to a decay of the emission with time. This can be eliminated with sufficient accuracy by taking the mean of the two curves. In the experiments with +160 volts there was a rapid fall of temperature, the extreme variation being  $63^{\circ}\text{C}$ ., which caused a greater relative difference between the outward and return curves. This again should be eliminated along with the time changes by taking the average. When this is done it is seen that the general march of the curve is the same as that of the average curve with +40 volts. This shows that the effect on the mean curve of a steady drift in the temperature is practically negligible; and it is important because it was found impossible to keep the temperature constant owing to lack of steadiness in the supply of current. Both of the above cases, however, are extreme samples; in nearly all the other experiments there was a drift of between ten and twenty degrees. In the experiments with almost all the other salts the conditions in the series of experiments with +40 and +160 volts were practically identical, except for the difference in voltage, and in nearly every case the curves were indistinguishable, except for a difference in the absolute value of the currents. In considering them it will, therefore, only be necessary to refer to a single voltage, except where there are special reasons for doing otherwise.

Returning to the mean curves for sodium sulphate, it will at once be observed that they are quite different from those obtained by the strip method. In the first place the emission is not sensitive to small changes in the pressure at low pressures. A change from 0.004 mm. to 0.15 mm. pressure only increases the emission from 28 to 31 divisions, whereas in an experiment by the strip method at a similar temperature an increase of pressure from 0.016 mm. to 0.15 mm. more than doubled the emission. Some typical cases are exhibited graphically in fig. 1. Curves 1 and 2 in this diagram were both obtained by the strip method at  $730^{\circ}\text{C}$ . In the case of curve No. 1, which gave a maximum ionization at a pressure of 20 mm., the specimen was comparatively fresh, whereas in the case of curve No. 2 it had been heated for a long time and at high temperatures. Although these curves differ considerably from one another, they both differ from No. 3 in being much more sensitive to changes of pressure at the lowest pressures.

When the pressure was increased in the tube apparatus the immediate response was in the direction of reduced emission. A slow increase subsequently occurred which carried the current to a higher steady value than that which it

Fig. 1.

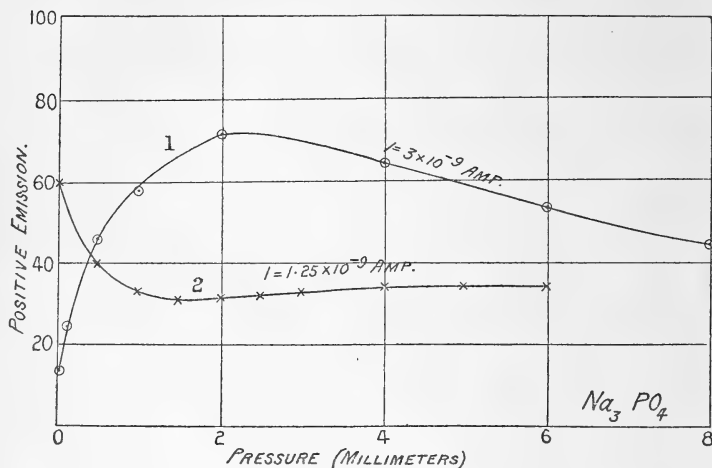


had at the lower pressure. This effect was always observed except at the very lowest pressures, and it occurred with all the salts investigated. The converse effect occurred on reducing the pressure; the emission first increased and then fell to a steady value. The effect with increasing pressure might conceivably be due to a reduction in the temperature of the surface of the salt produced by letting in the cooler air; but this seems unlikely when one considers the small amount of air let in at any one stage, and the fact that the heating apparatus was getting rid of one kilowatt of power, most of which, in all probability, went into the water-cooler. It is also difficult to see how an explanation along similar lines could account for the converse effect which occurs on reducing the pressure. Another explanation of these effects will be considered below.

*Tribasic Sodium Phosphate.*—The current-E.M.F. curves given by this substance were quite similar to those obtained in the two cases already described, the main difference being that there was still less variation from one pressure to another. The curves showing the variation with pressure, however, were

quite different, both from the curves given by sodium phosphate by the strip method and from all the curves given by sodium sulphate. Curve No. 2 on fig. 2 shows the mean curve with +40 volts. The mean curve with +160 volts

Fig. 2.



was practically identical with this except for a difference in the absolute values of the currents. The mean temperature during this experiment was  $775^\circ \text{C}$ . with a steady drop of  $15^\circ \text{C}$ . from the beginning to the end. Curve No. 1 (fig. 2) is taken from Horton's paper and was obtained at  $800^\circ \text{C}$ . by the strip method. His currents seem a little larger than mine after allowing for the different temperatures and size of apparatus, but he does not say which of the phosphates of sodium he used. The lowest pressure in the tube experiments was  $0.005 \text{ mm}$ . and the emission was greatest at this pressure. It fell rapidly to a minimum at  $1.5 \text{ mm}$ . and after that rose very slightly. In the strip experiments the emission is least at the lowest pressure, undergoes a rapid increase to a maximum at  $2.3 \text{ mm}$ . and then falls off slowly. The behaviour is almost the exact opposite of that given by the experiments with the tube.

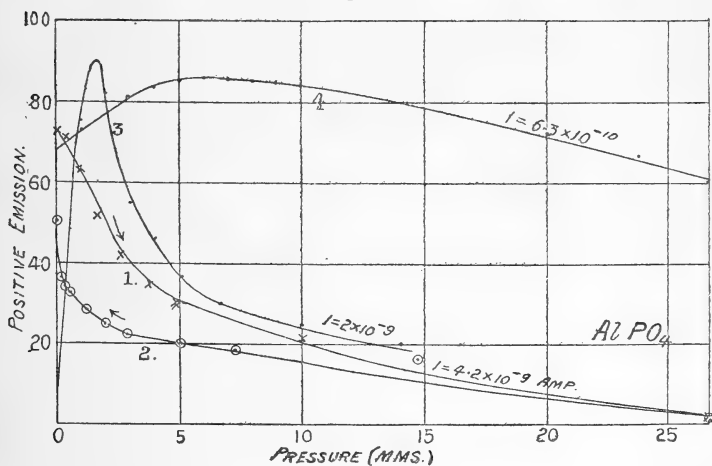
On taking down the apparatus after this experiment, the inner electrode was found to be covered with a thin layer of salt which had a fishy smell and deliquesced rapidly.

*Aluminium Phosphate.*—The salt used was supplied by Kahlbaum. A sample from the same stock was used by Mr. Davisson in his measurements of  $e/m$  for the positive ions

from this substance. According to Mr. Davisson's experiments the value of  $m/H$  for the carriers from this material was 22, indicating that they were atoms of sodium. The current-E.M.F. curves were similar to those already obtained, except that the straight part of the curve had a rather steeper slope and there was more variation from one pressure to another than the average. This might be explained if the central electrode were nearer to the platinum tube than usual.

Two current-pressure curves with +40 and +160 volts were taken at temperatures a little under  $800^{\circ}\text{C}$ . They were practically identical. The results of the one with +160 volts are exhibited in fig. 3. Curve 1 gives the currents with increasing, and curve 2 with diminishing, pressures. There was a gradual fall of temperature during this experiment from  $789^{\circ}\text{C}$ . to  $774^{\circ}\text{C}$ . Curve 3 is taken from Garrett's

Fig. 3.



paper and represents the emission as measured by the strip method at  $1005^{\circ}\text{C}$ . If the data were reduced to the same conditions I think my currents would be larger than those obtained by Garrett at all pressures. Curve 4 will be considered later.

The chief difference between curve 3 and the mean of curves 1 and 2 is in the behaviour at low pressures. The tube method shows no indication of the large increase to a maximum given by the strip method under these conditions. On the contrary there is a uniform diminution of the emission

as the pressure is reduced to atmospheric. At atmospheric pressure the current was less than  $10^{-9}$  ampere. The first explanation which occurred to me was that the actual pressures were not so low as those measured in the tube experiment owing to the evolution of gas in the apparatus and leakage through the iron tube under the influence of heat. This explanation does not appear to hold, however, for the measured pressures were as low as .005 mm. when the pump was working continuously, and it took several minutes for enough gas to accumulate after the pump was stopped to show a pressure of 0.1 mm. ; whereas the maximum observed by Garrett at  $1005^{\circ}$  C. was at about 1.6 mm. and would probably be at a still higher pressure at the lower temperature of these experiments. It is important also to remember in this connexion that the experiments with the empty tube had indicated that the gas which leaked through the hot steel crucible was probably small in amount compared with that evolved by the heated salt at these low temperatures, so that the larger leak at lower pressures is not likely to have been caused by the peculiar properties of such gases. On taking down the apparatus after this experiment there was no deposit in the inner electrode, but the apparatus had a faint smell reminding one of that of soot.

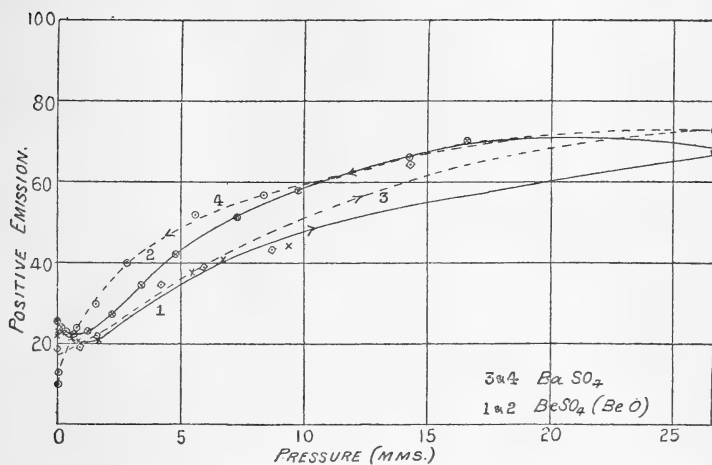
*Beryllium Sulphate*,  $\text{BeSO}_4$ .—Experiments were made on a specimen of this salt which was kindly furnished by Mr. Parsons and which was supposed to be especially pure from a chemical standpoint. The value of  $e/m$  for the positive ions was determined by Mr. Davisson and found to correspond to potassium. The emission investigated is presumably that from beryllium oxide since the sulphate loses  $\text{SO}_3$  and is converted into the oxide at high temperatures. The current-E.M.F. curves were similar to those given by aluminium phosphate.

The effect of pressure on the emission from beryllium sulphate is shown by the full curves in fig. 4. The actual values plotted were obtained with +40 volts on the tube, but precisely similar results were obtained with +160 volts. The temperature rose gradually from  $822^{\circ}$  C. to  $839^{\circ}$  C. during this experiment. The unit of current is  $2.5 \times 10^{-9}$  amp. The main features of the curves are a small drop in the emission with increasing pressure at low pressures leading to a minimum value in the neighbourhood of 1 mm., followed by a gradually diminishing rate of increase to much higher values at higher pressures. There is no indication of a pressure at which the emission is a maximum under 25 millimetres. Experiments were not made at pressures higher than this.



*Barium Sulphate*,  $\text{BaSO}_4$ .—In all the experiments with this substance exactly one gram of it was used. The specimen of salt first used was supplied by Kahlbaum. Davisson's experiments have shown that the positive ions emitted by

Fig. 4.



this substance are atoms of barium with a single electronic charge. The current-E.M.F. curves were similar to what would be obtained by taking the average of these given by the salts already examined.

The relation between positive emission and air-pressure below 25 mm. is shown by the dotted curve in fig. 4. The unit of current is  $2.5 \times 10^{-9}$  amp. and the temperature during this experiment varied only between  $760^\circ \text{C.}$  and  $762^\circ \text{C.}$  The mean curve is similar to that given by beryllium sulphate (or oxide) except for the absence of the minimum at about 1 mm. It will be observed that the ascending and descending branches cut one another. This was frequently observed with barium sulphate, but not with any other of the salts tried. This salt seemed to evolve less gas than most of those previously examined as it was possible to pump down to pressures as low as .001 mm.

*Barite*,  $\text{BaSO}_4$ .—It seemed desirable to test a sample of barium sulphate from some other source; so a specimen of the mineral barite from Hartz, Prussia, was examined. One gram of it, finely powdered, was placed in the bottom of the platinum tube. The mineral has not yet been analysed. It looked pure, but was not transparent.

In the previous experiments the length of time the salt had been heated before the observations were taken was not recorded. It varied from 4 to 8 hours, according to the convenience of the observer and the time required for steady conditions to be obtained. In the present experiments a record was kept of the time which elapsed in this way.

Current-E.M.F. curves were taken after about 10 hours' heating. They showed a better approach to saturation than any which had been obtained previously as the following numbers testify.

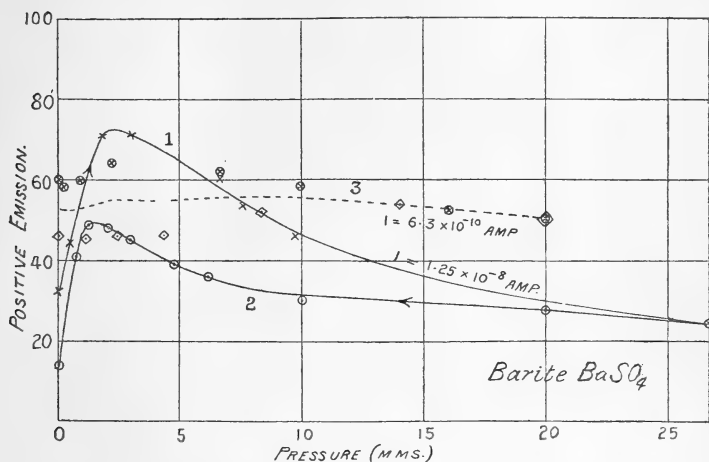
Voltage .....	0	40	80	120	160	200	240	320	400
Current, pressure } = 0.0015 mm. }	0	1	1.025	1.06	1.03	1.10	1.12	1.14	1.19
do. 0.8 mm. ....	0	1	1.03	1.11	1.13	1.21	1.24	1.42	1.60
do. 9.4 mm. ....	0	1	1.12	1.18	1.25	1.31	1.35	1.46	

The currents which are given in the three lower rows have been arbitrarily reduced to equality at 40 volts. The order of magnitude of the unit is  $10^{-7}$  amp. Although the temperature was only  $785^{\circ}$  C. in this experiment it was observed that there was a negative emission of about  $5 \times 10^{-7}$  amp. This negative emission is very much larger than the platinum alone could give rise to at that temperature, and it seems probable that the heating in a vacuum had partially converted the barium sulphate into barium oxide which was giving rise to the large negative emission which Wehnelt showed to be characteristic of that substance. It is curious that the positive emission should be easier to saturate in the presence of this large negative emission, but I have frequently noticed that the current saturates more easily after continued heating. This is one of several features of the relation between the current and electromotive force in the case of heated salts which seems worthy of further investigation.

The positive emission after the barite had been heated for 11 hours is shown in curves 1 and 2 of fig. 5. Curve 1, points thus,  $\times$ , corresponds to increasing, and curve 2, points thus,  $\odot$ , to diminishing pressures. The temperatures in this experiment fell steadily from  $783^{\circ}$  C. to  $772^{\circ}$  C. This curve is quite different from the one obtained with the chemical barium sulphate. I think, however, that the difference is due to the difference in the previous history rather than to the different composition of the material, as the same sample of barite later on gave a curve which was similar to those which had been obtained from the barium sulphate. Curves 1 and 2 show a greater sensitiveness to changes of pressure

at low pressures than has been observed in any other case by the tube method, but the sensitivity is still much less than that obtained in most cases by the strip method with the various salts which were tested by it.

Fig. 5.



At the end of the last experiment the thermionic current was  $1.75 \times 10^{-7}$  amp. when the apparatus was pumped right down to 0.002 mm. Air was let in to a pressure of 1 mm. when the emission increased to  $3.2 \times 10^{-7}$  amp. On increasing the pressure to atmospheric the steady emission was found to have diminished to  $5.5 \times 10^{-8}$  amp. When the air was pumped out again the emission remained fairly constant until a pressure of about 10 mm. was reached, when it fell off steadily until the value  $1.75 \times 10^{-8}$  amp. was reached at 0.004 mm. A current-pressure curve was then taken immediately and gave the following values :—

Pressure (mm.)	.....	0.004	0.66	1.63	2.9	5.7	8.3	20	9.4	7.75	4.48	1.83	0.87	0.04
Positive Emiss.	}	14	16	17	18	19	19	17	15	15	13	10.5	10	12
( $I = 1.25 \times 10^{-9}$ amp.)														
Actual Temperature...		775° C.					775° C.					775° C.		

The mean curve obtained from these numbers only varies from 13 to 17 between 0.004 and 25 mm., and exhibits a steady rise from 0 to 6 mm., after which it remains practically constant. The substance had been heated for about 13 hours at the close of the last experiment. It was now heated in a

vacuum for 14 hours more and a test made at  $797^{\circ}\text{C}$ ., which gave the following values for the mean curve :—

Pressure (mm.).....	·002	·5	1	2	3	4	5	6	8	10	16	25
Positive Emission	}											
( $1=6\cdot3\times10^{-9}$ amp.).		26	38	46	55	58	60	61·5	62	60	55	35

This curve has a flat maximum at 6 mm. pressure and is intermediate in character between the first curves and those given by barium sulphate prepared chemically.

Immediately after this experiment air was let in to atmospheric pressure, when the emission dropped to 4 divisions on the above scale of current. On reducing the pressure it rose slowly to 15·5 divs. at 15 mm., but part of this may be due to equilibrium not being fully attained at the lowest pressure. On further evacuation the current became steady at 15 divs. at 0·004 mm. A pressure curve was then taken which is shown in fig. 5. The ascending points are shown thus  $\otimes$ , and the descending points thus  $\diamond$ . The dotted curve represents the mean: it is practically a straight line parallel to the pressure axis. The temperature in this experiment was  $783^{\circ}\text{C}$ .

Several points stand out quite definitely as a result of these experiments with barite. After exposure to air at atmospheric pressure the emission is comparatively small *and varies very little with the pressure from atmospheric pressure down to 0·003 mm.* One experiment showed an increase and the other a decrease on evacuation from atmospheric pressure, but the change in both cases was small. When the power of emission has been reduced in this way it is recovered again by long continued heating at low pressure.

The most natural interpretation of these results is that the barium sulphate is decomposed by continued heating in a vacuum and forms a substance which has a greater thermionic activity. I am inclined to suspect that this substance is barium sulphide as the tubes usually smelt of sulphuretted hydrogen when they were taken down. If that is the case, the effect of heating in air at atmospheric pressure would be the reconversion of the sulphide to sulphate. On this view, the true emission from the sulphate is the smaller emission which is obtained after exposing to air at atmospheric pressure and which varies very little with the pressure of the gas in the apparatus.

*The effect of Hydrogen.*—If there is anything in the above view a greatly increased emission should be obtained by reducing the sulphate in an atmosphere of hydrogen. A

number of experiments were therefore made in this gas. Although the results obtained are very complicated they are quite clear as to the point that heating in an atmosphere of hydrogen greatly increases the emission. In the following descriptions the currents are in terms of scale divisions one division being equal to  $1.25 \times 10^{-9}$  amp.

At the commencement of the experiment the air was pumped down to a pressure of  $.003$  mm. and the emission was then 22 divisions. The temperature was  $800^{\circ}$  C. Hydrogen was then let in to a pressure of 11 mm. and the emission rose almost immediately to 110 divisions and then more slowly, so that at the end of 40 minutes it had become 268 divisions. The hydrogen was then pumped out, the current and pressure being observed from time to time. There was an increase with diminishing pressure to 5 mm. when the emission was 390 divisions. It then fell gradually to 114 divisions at  $0.003$  mm. More hydrogen was then admitted when it increased to a temporary maximum of 350 divisions at 7 mm. pressure. The decrease was very slight, however, and on admitting more hydrogen the emission began to increase again more rapidly than the pressure. At 224 mm. it had reached 3100 divisions. The temperature only varied  $3^{\circ}$  from  $800^{\circ}$  during these experiments. The pressure slowly fell a little after each admission of gas, showing that the hydrogen was being converted into water which was being absorbed by the phosphorus pentoxide bulb. After admitting hydrogen to a pressure of 348 mm. the apparatus was left for two hours. On returning, the temperature had fallen from  $798^{\circ}$  to  $768^{\circ}$ , the pressure was reduced to 323 mm., and the emission had increased to 6000 divisions. The hydrogen was then pumped out, when the emission fell to a minimum of 2100 divisions at 1500 mm. followed by a maximum of 5300 divisions at 20 mm. and a rapid drop thence to 145 divisions at  $0.005$  mm. Air was then let in to atmospheric pressure when the emission fell to 20 divisions. The temperature had dropped to about  $730^{\circ}$  by this time. On pumping out the air the emission rose slowly to a maximum of 53 divisions at 30 mm. from which it fell, slowly at first and then more quickly, to 15 divisions at  $0.006$  mm.

When the apparatus was taken down the cold electrode had been blackened by the sulphuretted hydrogen. The lower end was covered with a saline deposit, much discoloured, which smelt strongly of hydrogen sulphide. An examination of the substance left in the tube indicated that it was principally barium sulphide with some barium sulphate

and barium oxide and a trace of polysulphides. There was no evidence of the presence of sulphites or thiosulphates.

*General Survey of the preceding Experiments.*

The results which have been obtained are extremely complex and difficult to unravel. I think this is largely due to the very complicated chemical actions which take place at these high temperatures. Of the complexity of the chemical actions which occur there can be no question. For example, when the tube with the hot platinum electrode insulated on quartz was taken down, after an experiment in which sodium sulphate had been tested in air at low pressures, the following observations were made. The central electrode smelt strongly of  $\text{H}_2\text{S}$ . The lower end was covered with a black deposit and the upper end with a red salt. The crevices between the platinum and the quartz were full of a white salt which was yellow where it touched the platinum. The black and red deposits were mixed with a background of white deliquescent salt. All of these substances must have been formed by the action of the salt vapours on the hot platinum, as there was nothing on the central electrode when it was put into the tube.

To help towards a more comprehensive view of the phenomena rough data bearing on the absolute value of the currents obtained have been collected in the following table (pp. 696 & 697). The substance tested is given in the first column. The second column gives the least pressure at which observations could be made, and the third the value of the current at this pressure. The fourth gives the pressure of maximum emission where it occurred, and the fifth the value of the maximum emission. The sixth column gives the temperature at which the observations recorded in the preceding columns were made. The eighth column states whether the observations were made by the strip or tube method, and the tenth column gives the value of the highest observed rate of emission reduced roughly to equal areas, and a standard temperature of  $800^\circ\text{C}$ .

The numbers in column 10 are to be regarded as indicating only orders of magnitude on account of lack of precision in the data. The variation with temperature of the emission from these substances is not known, but it was assumed that fair results would be obtained by taking it to be the same as that of aluminium phosphate in each case. According to Garrett's observations the emission from this substance doubles for every  $30^\circ$  rise of temperature in the

neighbourhood of  $900^{\circ}\text{C}$ . The reduction to equal areas is a still less definite matter. It is not yet certain whether the emission is due to the salt directly or to the interaction with the platinum of vapours which it gives off. I think there is a considerable amount of evidence that the latter is an important factor. I have therefore reduced to equal areas of platinum surface and have taken the effective area of the platinum tube to be 60 sq. cm. In the case of the strips the area of both sides has been counted. The other observers do not seem to have recorded the area of the strip covered by the salt, but it is probable that if equal areas of salt were compared the values in column 10 would be altered relatively in favour of higher values for the platinum tube.

One of the most striking features of the numbers in column 10 is the comparatively small difference in the greatest currents given by the different salts when tested by the tube method. With the exception of pure aluminium phosphate, which will be considered below, the smallest maximum emission is given by  $\text{BeSO}_4$  (or  $\text{BeO}$ ) with  $14 \times 10^{-10}$  amp. and the largest by  $\text{BaSO}_4$  (barite, but probably due to  $\text{BaS}$ ) with  $190 \times 10^{-10}$  amp. If the emission after heating in air at atmospheric pressure is taken to be that characteristic of  $\text{BaSO}_4$  then this substance would be the least efficient with an emission of only  $7 \times 10^{-10}$  at  $800^{\circ}\text{C}$ . I have not found the phosphates to be especially efficient.

A comparison of the maximum currents obtained by the two methods indicates that the tube causes a greater emission than the strip when equal areas are compared. Horton's measurements with sodium phosphate are an exception in this respect, but the salt he used was, of course, a different specimen from that tested in the tube experiments. My experiments with trisodium phosphate gave much smaller currents at the same temperatures than those recorded by Horton for "sodium phosphate."

One advantage of testing the emission by two widely different methods such as those which have been described, and at the same time making tests on a number of different kinds of salts, is that it offers some chance of a separation of the physical from the chemical effects. One would expect that effects which were physical in their origin would depend upon the method of testing employed, but would be independent of the nature of the salt. Conversely effects which arose from chemical changes might be expected to vary considerably from one salt to another, but not to depend so much upon the method of testing employed.

1	2	3	4	5	6	7	8	9	10
Material.	Lowest Pressure, mm.	Thermionic Emission, amps.	Maximum Pressure, mm.	Maximum Emission, amps.	Temperature 0° C.	Observer.	Method.	Remarks.	Maximum emission under standard conditions, amps./cm. <sup>2</sup>
Platinum.	0.007	$1.5 \times 10^{-6}$	Emission independent of pressure.		984	Richardson.	Tube.	Air.	$3.9 \times 10^{-10}$
	0.004	$3.13 \times 10^{-7}$	8 (flat)	$6.25 \times 10^{-7}$	798	Richardson.	Tube.	Air.	$1.05 \times 10^{-8}$
	0.00003	$8 \times 10^{-13}$	20	$1.67 \times 10^{-11}$	730	"	Strip.	Air.	$1.2 \times 10^{-10}$
	0.0003	$2 \times 10^{-9}$	4	$3.5 \times 10^{-8}$	1005	"	"	Air.	$4 \times 10^{-10}$
	0.0003	$1.3 \times 10^{-7}$	0.2	$7.8 \times 10^{-7}$	1160	"	"	Air.	$2.0 \times 10^{-9}$
$\text{Na}_3\text{PO}_4$ .	0.005	$7.2 \times 10^{-8}$	1.5 (min.)	$3.7 \times 10^{-8}$	776	Richardson.	Tube.	Air.	$3.7 \times 10^{-8}$
	0.00018	$1.2 \times 10^{-10}$	2.3	$6 \times 10^{-9}$	730	"	Strip.	Air.	$2 \times 10^{-7}$
			2.3	$2.15 \times 10^{-7}$	800	Horton.	Strip.	Air.	$1.1 \times 10^{-6}$
Sodium Phosphate.			2.0	$1.27 \times 10^{-6}$	800	"	"	CO.	$6 \times 10^{-9}$
			No maximum.		793	Richardson.	Tube.	Air.	$3.6 \times 10^{-9}$
Aluminium Phosphate.	0.005	$2.3 \times 10^{-7}$	1.6	$1.8 \times 10^{-7}$	1005	Garrett.	Strip.		
			0.5	$9 \times 10^{-7}$	1115	"	"		





The effects which seem to depend rather on the mode of testing than the nature of the material employed are :—

1. By the strip method a very small emission occurs at very low pressures which increases rapidly with increasing pressure. The tube method makes the emission much less sensitive to variations in the pressure at low pressures, the changes being sometimes in one direction and sometimes in another.

2. In the tube experiments the *immediate* response to increasing the pressure is a diminution in the emission, followed later by the change which is characteristic of the steady end condition. The converse effect occurs on reducing the pressure.

3. The emission per unit area of the hot platinum seems on the average to be greater with the tube method than with the strip method of testing.

The chemical effects are evidently very involved. On the whole there is a greater tendency for the emission to be diminished with increasing pressure in the case of the phosphates than in the case of the sulphates. In the case of at least one of these substances, however, we shall see that the emission is not due to the substance itself but to something mixed with it. The emission from the reduction products of barium sulphate is greater than that from the sulphate itself. The emission from the latter probably varies very little with the pressure of the surrounding air.

#### *Observations on Aluminium Phosphate.*

It will be remembered that Sir J. J. Thomson found that this substance gave rise to a much greater emission of positive ions than a great number of representative salts which he tested under similar conditions. My experiments, however, do not indicate that the specimen of aluminium phosphate which I used was remarkable in this respect. This difference coupled with the fact, established by the experiments of Davisson mentioned above, that the carriers of the ionization from our specimen of aluminium phosphate had a value of  $m/H$  equal to 22, led to the view that the emission of positive ions ordinarily observed with aluminium phosphate is due, not to the salt itself, but to something mixed with it.

To test this view it seemed desirable to prepare aluminium phosphate, if possible, in a way which would ensure freedom from contamination with other inorganic impurities and especially with the salts of the alkali metals. There seemed a reasonable chance of this if the salt were prepared from

materials all of which had undergone distillation. This was done by the action of ammonia on a mixture of dry aluminium chloride with excess of orthophosphoric acid. The dry aluminium chloride and phosphorus pentoxide were supplied by Eimer and Amend and had been made in Germany. The orthophosphoric acid was prepared by boiling the phosphorus pentoxide in distilled water. The ammonia solution was analysed and contained 28 per cent. of  $\text{NH}_3$  and 0.0004 per cent. of non-volatile matter. It was added cold to the mixture of the solutions of aluminium chloride and orthophosphoric acid, which had a temperature of about  $40^\circ \text{C}$ . The mixture was stirred constantly and the ammonia was added until the precipitation was almost but not quite complete. The precipitate was thoroughly washed on the filter with boiling distilled water. It was divided into two parts, one of which was allowed to remain pasty and the other dried in an air oven at such a temperature that a piece of filter-paper placed over it was slightly charred at the edges after about two hours' drying.

0.2 gram of the dry phosphate, about the same amount as had been used in working with Kahlbaum's phosphate, was tested in the platinum tube apparatus in the usual way. It was found that it did not give rise to thermionic currents of the order of  $10^{-8}$  amp. until temperatures above  $1000^\circ \text{C}$ . were reached. The mean current-pressure curve at  $1050^\circ \text{C}$ . is given in fig. 3 (curve 4). Reduced to a temperature of  $800^\circ \text{C}$ . this would correspond to about  $1/150$  of the emission given by Kahlbaum's aluminium phosphate, which in the light of the work of other observers appears to have been small rather than the reverse. It is not even certain that this small emission was due to the aluminium phosphate itself as it was less than what would have been given by the platinum tube alone at the beginning of the experiments. No doubt the emission from the platinum had fallen, but there is no evidence to show how much.

The small emission from the pure aluminium phosphate is not due to its having been dried, for the paste was tested by the strip method and found to give a small emission. There was a measurable current during the early stages of the heating, but it soon died away to a very small value. A temporary emission of this character would have escaped notice in the tube experiments.

There are an enormous number of slightly different aluminium phosphates, according to the chemical handbooks, and the differences between the different samples might conceivably be due to differences in chemical constitution.

I think the fact that the phosphate with the large emissivity gave off ions for which  $m/H$  does not correspond to any of the chemical constituents of the substance rules this view out of court.

*Effect of an Electric Field on the Decay of the Emission.*

In 1906\* the writer showed that the rate of decay of the positive ionization from a new platinum wire is greater when the wire is positively charged than when it is charged negatively, indicating that the ionization is not due to the platinum alone, but to some foreign matter present in it, which is emitted in the form of positive ions and is thus unable to escape when the wire is negatively charged. This effect has recently been confirmed by Dr. W. Wilson†, who has adopted the explanation of it given by the writer.

This property, which in the case of pure platinum is confined to new wires, that is to say, to wires which have not been heated for a long period of time with a positive charge on them, occurs at low as well as high pressures. I have frequently found it to be well developed in a good vacuum. It also occurs in the case of heated salts, and I think it may be made use of to obtain valuable information about the mechanism of the emission in the case of these bodies. A number of experiments have already been made with aluminium phosphate which exhibit a very different behaviour in this respect under different conditions. In some cases the emission appears to be due to a vapour which is strongly ionized, whilst in other cases the ionization would seem to be very feeble. These experiments will be considered more fully in a later paper.

*General Discussion.*

While the results of the experiments which have been described are quite bewildering in their complexity when considered in detail, I think certain facts and principles are established by the evidence brought forward in this paper, which will prove to be of fundamental importance in the further development of this subject. In the first place all the direct evidence which appears to be trustworthy points to the view that the positive ions emitted by heated salts are metallic atoms. These are not necessarily atoms of the salt which appears to be under examination, but may be atoms of some other metal whose salts are present as an impurity.

\* Phil. Trans. A, vol. ccvii. p. 30 (1906).

† Phil. Mag. [6] vol. xxi. p. 636 (1911).

Until new direct evidence to the contrary is presented, I think it is necessary to accept as a fact the statement that the positive ions emitted by heated salts are charged metallic atoms.

Another proposition which it is necessary to admit the truth of is that the ionization emitted by heated salts is not always due to the salt which is believed to be under examination, but may arise from minute quantities of other substances which are present as impurities. The evidence in this direction in the case of aluminium phosphate appears to be overwhelming.

The points which remain to be considered are, I think, of a more speculative character. As far as the relative efficiency of the different salts in emitting positive ions is concerned it seems to the writer that what is required for a good emitter is a combination of volatility in the possible compounds formed together with high electro-positiveness of the metallic constituent. Thus barium sulphide, which is more volatile, is apparently more efficient than barium sulphate, and this in turn is more effective than barium oxide which gives a large negative but no positive emission when pure. In the series of the alkali metals the most electropositive are the most efficient emitters, and the same is true in the alkaline earth group. The zinc haloids are very efficient and they combine the qualities postulated. In discussing a question of this character it is of course necessary to rule out of court substances like aluminium phosphate which are not self emitting.

A large number of facts which are otherwise very difficult to explain can be reconciled by the view that the ionization, in certain cases at least, is not emitted directly from the heated salt but by the action on the platinum of vapours which the salt evolves. In the first place this would explain the very small ionization at very low pressures which is observed by the strip method. The vapours diffuse away from the strip before they have time to get ionized. The effect of increasing the gas pressure is to prevent the vapour from diffusing away from the strip, and so the ionization increases. In the tube method the vapours are unable to diffuse away from the hot platinum, and so there is very little change of the emission with changing pressure at low pressures. It is very difficult to account for this great variation with the pressure at low pressures, obtained by the strip method, on any other view except by falling back on chemical changes. These would have to act in the same way in such different gases as air, oxygen, hydrogen, carbon monoxide, and carbon dioxide, for such different salts as sodium phosphate and sodium sulphate and the impurities

present in aluminium phosphate, and at the same time behave quite differently for all salts and gases in the tube experiment from what they do in the strip experiment.

This view would also account for the sudden apparent drop in the emission when the pressure was increased in the tube experiment. The vapour in the tube would be compressed into the bottom and so would have less platinum surface to act on. The converse phenomenon on lowering the pressure is also readily explained in this way. The instantaneous effect on lowering the pressure is smaller than the opposite effect when the pressure is raised, as it should be.

The greater effect, even when reckoned per unit area of platinum, as obtained by the tube method is readily explained in this way, and is quite incomprehensible on the opposite view. The smallness of the electrode compared with its surroundings enables the vapour to diffuse away very readily in the strip experiment, whereas convection currents carry it up against the hot platinum walls in the tube experiment.

The very varied curves obtained by changing the pressure at constant temperature with different salts and with the same salt after it has been treated in different ways seem to be symptomatic of chemical changes. By that, I mean that they are probably accompanied by changes in the composition of the material which correspond to the curves in some way. This gives a very natural explanation of the variability and complexity of the curves, as the chemical actions are probably quite different in the different cases and extremely complex in every case. One of the difficulties of the subject is that practically nothing is known about the mechanism of chemical reactions at high temperatures. All the information available relates to those of the end products which happen to be formed in comparatively large quantity.

The statement that the pressure changes are in all probability symptomatic of chemical action is quite apart from the important question as to whether chemical actions of the ordinarily recognized types at high temperatures are accompanied by the emission of positive ions. The very vigorous emission observed when barite was being attacked by hydrogen tends to support this view, but it may have been that the hydrogen was facilitating the formation of some relatively volatile compound of barium and thus enabling it to reach the platinum surface. The action of water on sodium sulphate is another case of the same kind. There is, of course, no doubt that ionization is an important feature of many chemical actions at high temperatures, the cases of flames, the oxidization of phosphorus, and the action of phosphorus on hot platinum furnishing well known examples.

The chemistry of the emission of positive ions from salts is, however, still unsolved. The reaction might for example be a catalytic one of the type



where E stands for a negative electron which goes over to the platinum and carries the current, the metal (barium in this case) being liberated by ordinary chemical actions which do not involve the transference of electric charge. Personally, however, I am inclined to suspect that in some way ions play a very fundamental and important part in chemical actions at high temperatures, just as they do in solutions at ordinary temperatures.

On the whole there is no reason for supposing that there is any essential difference between the mechanism of the large positive emission from freshly heated metals and that observed with salts. They both have the same general characteristics, namely: (1) an initial exponential decay with time followed by a slowing off<sup>\*</sup>; (2) occasionally the variation with time is more complicated, an intermediate rise to a maximum being observed<sup>†</sup>; (3) the decay with time is quickest when the body is positively charged and is retarded by a negative charge<sup>‡</sup>; (4) both vary with the temperature according to a formula of the type  $a\theta^{\frac{1}{2}}e^{-b/\theta}$ , where  $a$  and  $b$  are constants<sup>§</sup>; (5) in neither case is there any simple relation between chemical action and thermionic emission<sup>||</sup>; and (6) the kinetic energy of the thermions is much the same in both cases<sup>¶</sup>.

The very small ionization which is observed when an "old" platinum wire is heated in different gases<sup>‡</sup> and which is a function of the pressure is, I think, quite different from anything which has hitherto been observed with salts. It seems probable that in this case the positive ions will turn out to be atoms of the surrounding gas, but all the existing evidence as to their nature is indirect. The difficulty in measuring the value of  $e/m$  for them lies in the smallness of the currents.

In conclusion I wish to thank my assistant, Mr. E. S. Taylerson, and my former assistant, Mr. Cornelis Bol, for their help in taking the observations.

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Princeton, N. J.

\* O. W. Richardson, *Phil. Mag.* [6] vol. vi. p. 80 (1904).

† O. W. Richardson, *C. R. Liège*, p. 50 (1905).

‡ O. W. Richardson, *Phil. Trans. A.* vol. ccvii. p. 1 (1906).

§ O. W. Richardson, *B.A. Reports*, Cambridge, 1904, p. 472.

|| R. J. Strutt, *Phil. Mag.* [6] vol. iv. p. 98 (1903).

¶ F. C. Brown, *Phil. Mag.* [6] vol. xviii. p. 649 (1909).

LXVII. *Note on the Diffusion of Neon through Hot Quartz.*  
 By O. W. RICHARDSON, *Professor of Physics*, and R.  
 C. DITTO, *Fellow in Physics, Princeton University* \*.

IN the course of some experiments which were undertaken to try to detect the presence of the heavier inert gases (xenon, krypton, argon, and neon) in minerals, we have observed that neon diffuses through red-hot quartz tubes. The possession of a similar property by helium has been known for some time, and appears to have been observed first by A. Jacquerod and F. L. Perrot †.

The method originally adopted consisted in heating the mineral in a closed silica-ware tube, initially exhausted. After the heating, the gas evolved was drawn off into a large exhausted reservoir. It was subsequently compressed into another heated quartz tube containing metallic calcium. Both the calcium and the mineral were heated to a temperature of about 1000° C. After exposure to the hot calcium, the gas was forced into a narrow capillary tube, where its spectrum could be examined by means of a Hilger wave-length spectroscop. Our experience is that hot calcium absorbs all the chemically active gases completely except hydrogen. We tried different temperatures between 800° C. and 1200° C., but always found that the calcium hydrogen compound exerted a dissociation pressure which, though minute, was large enough to be troublesome. We could not use higher temperatures on account of the silica-ware tubes becoming soft and collapsing under the atmospheric pressure. The hydrogen contamination was got rid of by forcing the gas into a small tube provided with a platinum tube heated by an electric current. The hydrogen diffused out through the hot platinum and burnt in the air of the room. These processes were gone through until we got a good clean spectrum showing the mercury lines and the lines of the inert gases present. As a rule the primary hydrogen lines were also visible, but not always.

The presence of neon in our apparatus was first noticed when a specimen of witherite from Northumberland, England, had been heated for a long time. We subsequently succeeded in proving that this mineral did not give off neon, and then tried the experiment with a new silica-ware tube which did not contain, and never had contained any foreign substance. After the exhausted tube had been heated for about one hour the gas was drawn off and examined. It was found to give

\* Communicated by the Authors.

† *Comptes Rendus*, cxxxix. p. 789 (1904).



a faint "blue argon" spectrum with the yellow helium line. After about three hours' heating the helium spectrum was fully developed, and the strong neon line at 5852 was well marked. The tube was then left hot all night. Next morning the helium and neon spectra were both quite strong, all the prominent neon lines being easily recognized. We could not be certain of any increase in the intensity of the blue argon spectrum which was present, either in this or in other similar experiments. This is important since it proves that the helium and neon had not leaked into the apparatus through the sealing-wax joints which connected to the two quartz tubes. In that case the argon spectrum should have increased proportionately with the others. This possibility is also excluded by the fact that the helium and neon present in the air cannot be detected spectroscopically in presence of the very large excess of argon which accompanies them. We have tested this question several times very carefully by examining the spectrum of the inert gases of the atmosphere under conditions similar to those which prevailed during the other experiments. We were never able to detect even the strongest helium and neon lines. The faint argon spectrum which was observed arose in all probability from the trace of air absorbed by the walls of the tubes before the heating commenced.

It is clear from these experiments that neon diffuses through quartz at about  $1000^{\circ}\text{C}$ ., but its coefficient of diffusion is smaller than that of helium. This follows since the helium is visible first, although there is about ten times as much neon as helium present in the atmosphere. Of course helium is more sensitive to the spectroscopic test than neon, but it does not seem likely that this will account for the facts, as the strong neon line appears at about the same time as the weak helium lines, in spite of the disparity in the amounts of the two gases present in the atmosphere. Arguing from the general similarity in the properties of the inert gases, it would seem likely that argon also would diffuse through hot quartz. If it does, the coefficient of diffusion must be very small, otherwise accumulation of argon would certainly have been observed in these experiments. This question is by no means easy to test experimentally, as there is always the possibility that a minute accumulation of this gas might arise from defective airtightness of the apparatus.

It seems likely that an easy method of measuring the amount of helium and neon in the atmosphere might be based on this property of diffusion through heated quartz. By attaching a quartz tube heated to a constant temperature to

a large reservoir, and observing the quantity of inert gas which had accumulated after a series of suitable intervals of time, it would in all probability be possible to deduce from an examination of the results, not only the final equilibrium amount of helium and neon together, but also the quantities of the two individually, as well as their coefficients of diffusion.

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LXVIII. *The Induction-Coil.* By E. TAYLOR JONES, D.Sc.,  
*Professor of Physics in the University College of North  
Wales, Bangor, and D. E. ROBERTS, B.Sc., Fellow of the  
University of Wales* \*.

[Plates XII. & XIII.]

THE experiments described in the present paper were made with the object of determining the elements (periods, amplitudes, damping-factors, and phases) of the two electrical oscillations which are set up in the secondary of an induction-coil when the primary current is interrupted, and of calculating hence the maximum value of the secondary potential and the potential at any time during the oscillations.

The principal difficulties connected with the calculation of the secondary potential of an induction-coil are (1) the determination of the effective self- and mutual-inductances of the coils, (2) the determination of the capacity of the secondary coil; the first owing to the want of proportionality between magnetic induction and magnetizing force in the iron core, the second owing to the smallness of the capacity and to the fact that the capacity is distributed along the coil. Some attempt was made in the experiments described below to overcome these difficulties, but there are other circumstances, including condenser losses, hysteresis, and irregularities in the working of the interrupter, which will have to be taken into account, or avoided, before a complete solution of the induction-coil problem can be reached.

The papers of Oberbeck †, Walter ‡, and Lord Rayleigh §, on induction-coil potentials are well-known and are therefore only mentioned here.

\* Communicated by the Authors.

† Oberbeck, *Wied. Ann.*, lxii. p. 109 (1897); lxiv. p. 193 (1898).

‡ Walter, *Wied. Ann.*, lxii. p. 300 (1897); lxvi. p. 623 (1898).

§ Rayleigh, *Phil. Mag.*, ii. p. 581 (1901).

General Description of the Method.

In a former communication one of us\* arrived at the following expression for the difference of potential at the terminals of the secondary of an induction-coil at any time  $t$  seconds after a current  $i_0$  is interrupted in the primary:—

$$2V_2 = \frac{Mi_0T}{(T^2 - T'^2)\cos\delta} e^{-\frac{t}{T}\left(\frac{\theta_1 + \theta_2}{2} - \beta\right)} \sin\left(\frac{t}{T} - \delta\right) \\ - \frac{Mi_0T'}{(T^2 - T'^2)\cos\delta'} e^{-\frac{t}{T'}\left(\frac{\theta_1 + \theta_2}{2} + \beta\right)} \sin\left(\frac{t}{T'} - \delta'\right), \quad \dots (1)$$

where  $M$  is the mutual inductance of the primary and secondary coils,

$$\theta_1 = \frac{1}{2}R_1C_1, \quad \theta_2 = \frac{1}{2}R_2C_2,$$

$1/2\pi T$  and  $1/2\pi T'$  are the frequencies of the two oscillations calculated from the well-known expression for coupled circuits

$$8\pi^2n^2 = \frac{1}{1-k^2} \left[ \frac{1}{L_1C_1} + \frac{1}{L_2C_2} \pm \sqrt{\left\{ \left( \frac{1}{L_1C_1} - \frac{1}{L_2C_2} \right)^2 + \frac{4k^2}{L_1C_1L_2C_2} \right\}} \right], \quad \dots (2)$$

$k$  being the coupling coefficient  $M/\sqrt{L_1L_2}$ .

The quantity  $\beta$ , and the phase-angles  $\delta$ ,  $\delta'$ , are to be calculated from the constants of the circuits as described in the former paper above referred to.  $R_1$ ,  $R_2$ ,  $C_1$ ,  $C_2$ ,  $L_1$ ,  $L_2$  are the primary and secondary resistances, capacities, and self-inductances.

In the paper referred to the above expression (1) was worked out for an *air-core* induction-coil with various condensers in the primary and secondary circuits, and the curve of secondary potential plotted from the results. The curve was also obtained photographically in each case by means of an electrostatic oscillograph, and was found to agree closely in its general form with the curve calculated from (1). The differences were mainly in the damping factors, and these discrepancies probably arose from losses in the primary condensers.

Strictly speaking, the expression (1) is not applicable to a coil with an iron core, owing to the variable permeability of iron; all that can be expected is that suitable mean values

\* E. T. Jones, Phil. Mag. January 1909, p. 28. This expression for the secondary potential was obtained by an application of Drude's 'Theory of the Oscillation Transformer,' *Ann. der Physik*, xiii. p. 512, 1904.

of the inductances may be found which will serve for the evaluation of the periods and amplitudes during at least a portion of the time of discharge. This was borne in mind in the experiments described below, and it was intended as far as possible to determine the mean inductances corresponding to the early portion of the discharge, since this portion includes the maximum secondary potential which is the quantity of greatest importance in an induction-coil.

The inductances of the primary and secondary coils were determined by electrical oscillation methods; a condenser of known capacity being connected to the primary (or secondary) coil, and the curve of secondary potential being photographed and measured by methods which have been described in detail in former papers\*.

It was thought that by measuring that portion of the damped oscillation-curve in which the current amplitude was approximately the same as in the early part of the double-period discharge, appropriate mean values of the inductances would be obtained, since the iron core passed through the same series of magnetic states in both cases. It was scarcely to be expected that this plan would lead to very accurate results, but it was hoped that it would suffice for the purposes of an approximate estimation of the secondary potential.

The coupling coefficient of the two coils was determined by finding the period of the oscillations of the secondary circuit, connected to a condenser, with the primary open and closed. The ratio of the squares of these periods is then  $(1-k^2)$ .

The value of the expression (1) was worked out for two induction-coils, a 12-inch spark coil by Max Kohl, and an 18-inch coil by the same maker. In the experiments with the smaller coil a condenser was connected to the terminals of the secondary coil; otherwise the secondary capacity would have been so small that one of the oscillations would be too rapid to be accurately recorded by the oscillograph. In the case of the larger coil it was unnecessary to connect a condenser to the secondary, but the primary capacity was larger than is generally employed with induction-coils.

In these experiments the electrostatic oscillograph was provided with a steel strip under great tension in order to bring the amplitudes of the curves down to moderate dimensions. The metallic parts of the instrument were well sheathed in ebonite, and the terminals well separated, in order to prevent sparking.

\* E. T. Jones, *loc. cit.* pp. 33-35; and Phil. Mag. August 1907.

The interrupter consisted of a copper rod making contact with the interior of an iron vessel containing petroleum. The rod was raised automatically, as the reflected rays of light were crossing the photographic plate, by a lever placed beneath the rotating mirror.

*Experiments with a Condenser in the Secondary Circuit.*

When a condenser is connected to the terminals of the secondary, the capacity of the secondary coil only comes in as a small correction, and it is unnecessary to know its value very accurately. It consists partly of the internal capacity, depending upon the capacity of one section of the coil on the next and upon the number of sections, and partly of the external capacity which depends upon the position of the coil with respect to other bodies and especially with respect to the primary coil. The methods by which these capacities were determined were described in a previous communication\*.

*Case I.*—In the first experiment with the smaller induction-coil the primary was drawn out of the secondary until the curve of secondary potential, as shown by the oscillograph, had a simple and well-marked form, corresponding probably to some simple ratio between the two frequencies of oscillation. This case was intended as a preliminary test of the method.

The photograph is shown in Plate XII. fig. 8. The current broken in the primary circuit was 5.05 amperes, and the ordinate of the curve represents the square of the secondary potential at any subsequent time. The curve was photographed for four different values of the primary current  $i_0$  ranging from 2.8 to 5.05 amperes, and the general form of the curve was the same in all, only the amplitude varying with the current. The amplitude of the first wave in each was measured on the negative with a travelling microscope and the values found were, within 4 per cent., proportional to the squares of the primary currents.

The lower curve in the photographs represents the oscillations of a 768 tuning-fork photographed simultaneously. Immediately after these curves were obtained another curve was photographed showing the secondary potential for an *air-core* induction-coil with known capacities and inductances in its circuits. This curve was similar to one of those discussed in the previous paper above referred to, and to which the expression (1) may be assumed to apply. By

\* E. T. Jones, Phil. Mag., August 1907, p. 248.

both measuring and calculating the maximum amplitude in this curve the electrometer may therefore be standardised.

The iron-cored induction coil was again connected to the oscillograph and photographs obtained for the purpose of measuring the primary and secondary inductances, the coupling coefficient, and the capacities if these were not already known. The values of these constants in the present case were as follows :—

$$L_1 = 0.2342 \text{ henries.}$$

$$L_2 = 258.3 \quad ,,$$

$$M = 1.811 \quad ,,$$

$$k^2 = 0.5424$$

$$C_1 = 15.95 \text{ microfarads.}$$

$$C_2 = 0.0004748 \quad ,,$$

This value of  $C_2$  includes the capacity of the electrometer and of the secondary coil. The resistances of the primary and secondary coils were 0.32 and 14000 ohms.

The two frequencies of oscillation, calculated by (2), were

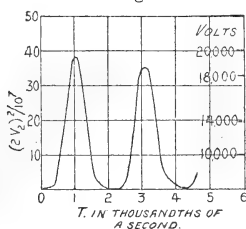
$$n_1 = 237.4, \quad n_2 = 737.0,$$

and the expression (1) for the secondary potential, taking the primary current  $i_0$  as 5.05 amperes, becomes in volts

$$\begin{aligned} 2V_2 = & 15230 e^{-6t} \sin(86.53t - 0.55) \\ & - 4910 e^{-68.15t} \sin(266334t - 1.72), \end{aligned}$$

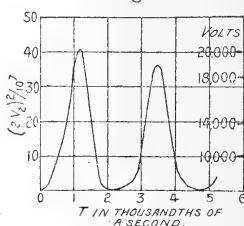
in which  $t$  is the time in seconds after the interruption of the primary current, and the angles are given in degrees. This was worked out for a number of values of  $t$ , the results squared and plotted in a curve the early portion of which is shown in fig. 1.

Fig. 1.



$$\begin{aligned} n_1 &= 237.4, \quad n_2 = 737.0, \\ i_0 &= 5.05 \text{ amp.} \end{aligned}$$

Fig. 2.



$$\begin{aligned} n_1 &= 219.8, \quad n_2 = 642.3, \\ i_0 &= 4.02 \text{ amp.} \end{aligned}$$

The agreement between this curve and the photograph in

Plate XII. fig. 8, is evidently sufficiently close to justify the application of the method to the present case. The damping of the waves is much greater in the photograph than in the calculated curve. This is also the case in the other experiments described below, and is to be expected since the only cause of damping taken into account in the calculation is that which arises from the resistances of the circuits.

The calculated maximum value of the secondary potential is 19650 volts, and the amplitude of the first wave in the photograph is 0.9276 cm. Now the standardising curve obtained with the air-core coil showed that a deflexion of 0.3032 cm. in the photograph corresponds to 10200 volts. Hence taking the deflexion as proportional to the square of the potential, the amplitude of the first wave represents a maximum potential of 17850 volts.

When it is remembered that the damping due to hysteresis and condenser losses have been entirely neglected, the agreement between the calculated and observed values of the maximum secondary potential is perhaps as close as could be expected.

*Case II.*—This case is similar to the first except that the primary coil with its iron core was placed further inside the secondary in order to increase the secondary self-inductance and the coupling coefficient. The secondary capacity (a variable condenser with paraffin-oil dielectric) was adjusted so as to give a form of oscillograph curve slightly different from that of *Case I.* The constants of the circuits were:—

$$L_1 = 0.2331 \text{ henries.}$$

$$L_2 = 428.1 \quad ,,$$

$$M = 2.436 \quad ,,$$

$$k^2 = 0.5949$$

$$C_1 = 15.95 \text{ microfarads.}$$

$$C_2 = 0.000499 \quad ,,$$

$$R_1, R_2 \text{ as before.}$$

The frequencies, calculated by (2), were

$$n_1 = 219.8, \quad n_2 = 642.3,$$

and, with  $i_0 = 4.02$  amperes, the expression for the secondary potential in volts is

$$2V_2 = 15320 e^{-5.46t} \sin(79146t - 0.51)$$

$$- 5247 e^{-51.85t} \sin(231221t - 1.49).$$

The curve representing the square of this expression is shown in fig. 2, the corresponding photograph in Plate XII. fig. 9, and again there is close agreement in the form of the curve.

The maximum secondary potential (calculated) is 20085 volts, the observed value (by comparison with the curve given by the air-core coil) 17250 volts.

*Case III.*—The primary coil was placed fully inside the secondary so as to give the maximum values of the secondary self-inductance and the coupling coefficient. Owing to sparking between the plates of the oil condenser this was replaced by a leyden-jar. The constants for this case were:—

$$L_1 = 0.2303 \text{ henries.}$$

$$L_2 = 513 \quad ,,$$

$$M = 3.197 \quad ,,$$

$$k^2 = 0.8643$$

$$C_1 = 15.95 \text{ microfarads.}$$

$$C_2 = 0.001051 \quad ,,$$

$$R_1, R_2 \text{ as before.}$$

The ratio of the frequencies was considerably greater than in the previous cases, their values being

$$n_1 = 170.1, \quad n_2 = 908.8.$$

With a primary current of 8.5 amperes the expression for the secondary potential is

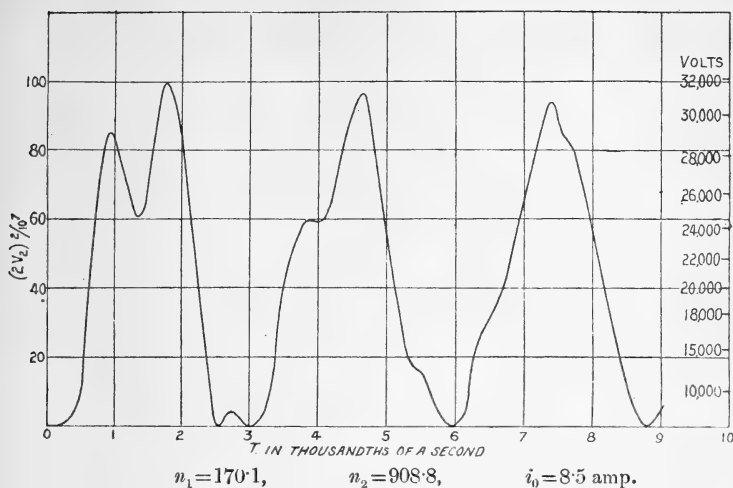
$$2V_2 = 30090 e^{-6.217t} \sin(61232t - 0.55) \\ - 5640 e^{-145.6t} \sin(327157t - 2.9).$$

The curve representing the square of this expression is given in fig. 3, and the corresponding photograph in Plate XII. fig. 10. Though there are differences in detail, in general form the resemblance between the two curves is close, and there is also good agreement, in this as well as in all the other cases, between the calculated and observed values of  $t$  at which the potential is zero. The calculated value of the maximum secondary potential is 31730, the observed value 26500 volts.

The greatest spark-length observed in this case between two brass spheres, each 2 centimetres in diameter, was 8.5 millimetres.



Fig. 3.



*Case IV.*—This differs from the last only in the use of a smaller capacity in the secondary circuit, its value being  $\cdot 0002213$  microfarad. The frequencies were

$$n_1 = 230.2, \quad n_2 = 1444.7,$$

and with  $i_0 = 6.75$  amperes the secondary potential is given by

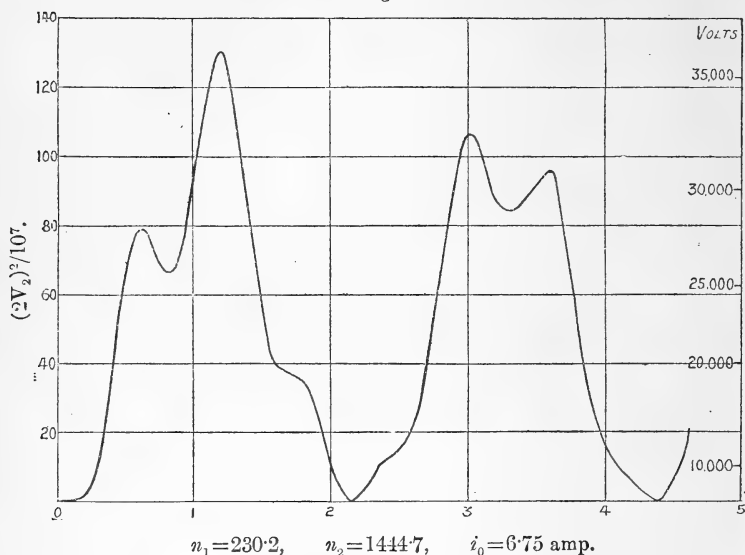
$$2V_2 = 32411 e^{-4.884t} \sin(82888t - 0.29) \\ - 5168 e^{-145.6t} \sin(520086t - 1.82).$$

The maximum value of this expression, which occurs at the second peak of the curve, is 36060 volts. The curve is shown in fig. 4 (p. 714).

Several photographs were taken for this case, and though similar in their general features they differed considerably from one another in detail. Sometimes the first peak was equal to or higher than the second, sometimes the peak in the second principal wave was higher than both maxima in the first. These differences arise apparently from irregularities in the working of the interrupter, which seem to affect chiefly the amplitude and phase of the more rapid oscillation. The photograph in Plate XII. fig. 11 shows the type which occurred most frequently. By comparison with the air-core coil the highest point of the curve was found to correspond to a secondary (observed) potential of 27560 volts.

The greatest sparking-distance between the two spheres under the circumstances of this experiment was found to be 1 centimetre.

Fig. 4.



It will be observed that in all the above cases the calculated value of the secondary potential is considerably greater than the observed value, and that the percentage difference increases with the potential.

#### *Experiments with no Condenser in the Secondary Circuit.*

If the condenser is removed from the secondary circuit of the smaller induction-coil, one of the oscillations becomes too rapid to be faithfully recorded by the oscillograph. The 18-inch spark coil was therefore used for the three following cases, its secondary having much greater self-inductance and capacity.

In order to work out the expression (1) for these cases it is necessary to know the value of the effective capacity of the secondary coil with greater accuracy than was required in the former cases. After several methods had been tried for the determination of this quantity, the following was finally

adopted. The condenser having been disconnected from the primary circuit, a current was passed through the primary coil and the curve of secondary potential, produced at its interruption, was photographed. Under these circumstances the oscillations of the system depend only on the constants of the secondary circuit, and should give the value of the product of the self-inductance and capacity of the secondary coil. The photograph showed, in fact, a single damped oscillation with period lengthening as the oscillations died away owing to the variation in the permeability of the core. The period was measured in the early part of the curve, where the amplitude is large, and was found to be  $\cdot 001763$  sec. Taking this as being equal to  $2\pi\sqrt{L_2C_2}$ , we have

$$L_2C_2 = 0\cdot787 \cdot 10^{-7}.$$

A condenser, of small known capacity  $C_2'$ , was then connected to the secondary coil and the period of this circuit, with the primary open, determined. This gives in the same way the value of  $L_2(C_2 + C_2')$ . From these two results the values of  $L_2$  and  $C_2$  can be determined. The values so found were  $L_2 = 2350$  henries,  $C_2 = \cdot 0000335$  microfarad. These values were used in working out the expression (1) for the following three cases. It may be noticed, however, that it is not so important to know the values of  $L_2$  and  $C_2$  separately as it is to know their product;  $C_2$  occurs separately only in the damping factors of the two oscillations represented by (1).

The self-inductance of the primary coil was determined by connecting to it the largest capacity available ( $20\cdot73$  microfarads), and photographing the curve of secondary potential produced at the interruption of a current in the primary. The curve obtained shows a double oscillation; but, since  $L_1C_1$  is much greater than  $L_2C_2$ , one of the oscillations has a much longer period than the other, and it is not difficult to determine the frequency of the slower oscillation from the photograph. On substituting in the expression (2) we obtain the value of  $L_1$ .

As the potentials obtained in the following experiments were higher than those in the former cases, the oscillograph was made less sensitive by withdrawing the attracting plate to a greater distance from the steel strip. To prevent sparking inside the instrument the attracting plate was enclosed in a thicker sheath of ebonite. The distance of the edge of the plate from the strip was about 7 mm.

Case V.—The constants for this case were :

$$L_1 = 0.1974 \text{ henries.}$$

$$L_2 = 2350 \quad ,,$$

$$C_1 = 15.95 \text{ microfarad.}$$

$$C_2 = .0000335 \quad ,,$$

$$k^2 = 0.8142.$$

$$M = 19.44 \text{ henries.}$$

$$R_1 = 1.90 \text{ ohms.}$$

$$R_2 = 38000 \quad ,,$$

$$i_0 = 4.3 \text{ amperes.}$$

The expression (2) gives for the frequencies

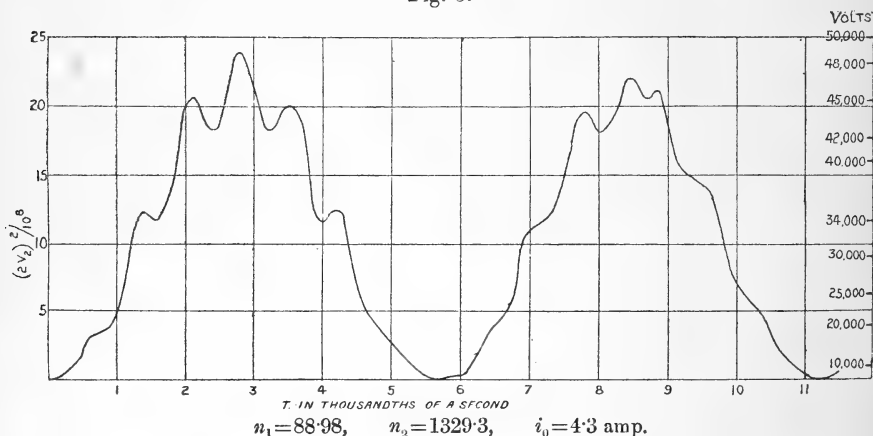
$$n_1 = 88.98, \quad n_2 = 1329.3.$$

By (1) the secondary potential is

$$\begin{aligned} 2V_2 = & 46950 e^{-4.654t} \sin(32033t - 0.05) \\ & - 3143 e^{-62.72t} \sin(478548t - 0.8). \end{aligned}$$

The curve representing the square of this expression is shown in fig. 5, and its maximum value is 48960 volts. The

Fig. 5.



photograph is given in Plate XIII. fig. 12, but it should be stated that the amplitude of the short wave varied considerably in different photographs, it being sometimes larger, sometimes smaller than is here shown. As in some other cases, these variations appear to arise from irregularities in the action of the interrupter.

The oscillograph was standardised in this and the two following cases, not directly with the air-core coil, but with the coil and condensers used in Case III., the greatest deflexion for a current of 8.5 amperes in that case being taken as representing 26500 volts. A comparison of the curves leads to 39480 volts as the greatest observed value of the secondary potential, which is again considerably below the calculated value.

The sparking-distance between the two spheres with the same primary current was found to be 1.6 centimetres.

*Case VI.*—In order to approximate more closely to the ordinary working conditions of an induction-coil, the primary capacity was now considerably reduced in value. This has the effect of increasing the secondary potential, and at this stage it was noticed that at high potentials a brush discharge took place freely between the ebonite sheath enclosing the attracting plate of the oscillograph and other parts of the instrument. The attracting plate and its connecting rod were therefore provided with still thicker coverings of ebonite, and the terminals of the instrument were removed to a greater distance from each other, in order to diminish as far as possible the leakage due to this cause.

The primary capacity was in the present case 3.89 microfarads, which gives, by (2), using the values given under Case V. for the other constants of the circuits,

$$n_1 = 174.4, \quad n_2 = 1371.$$

The expression for the secondary potential in volts is

$$\begin{aligned} 2V_2 = & 21650 i_0 e^{-4.14t} \sin(62770t - 0.1) \\ & - 2753 i_0 e^{-65.26t} \sin(493452t - 0.83), \end{aligned}$$

where  $i_0$  is the primary current in amperes. The curve representing the square of this expression was drawn for  $i_0 = 2.25$  amperes, and is shown in fig. 6 (p. 718).

Photographs were taken at the interruption of various currents in the primary circuit. One of these is shown in Plate XIII. fig. 13. The curves obtained were all of the same type, only the amplitude varying with the primary current. The greatest ordinate in each photographic curve was measured and compared with that of the standardising curve. The results are contained in Table I., in which the first column contains the values of the current interrupted in

the primary circuit, the second the maximum potential calculated by (1), the third the maximum potential deduced by measurement of the plates.

Fig. 6.

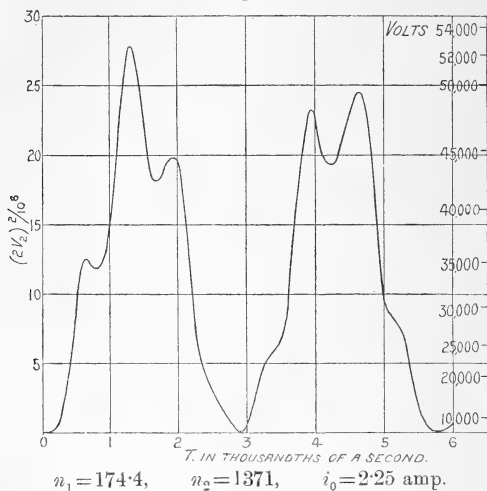


TABLE I.

$i_0$ , amperes.	Maximum Potential in volts.	
	Calc.	Obs.
2.64	61910	72220
3.16	74110	84110
3.90	91460	101070
4.44	104120	118560
5.10	119600	132940

The greatest spark-length observed between the two spheres with the current of 5.1 amperes, was 7.3 centimetres.

The observed value of the secondary potential is in this case greater than the calculated value. Probably the calculated value is too small, owing to the fact that the expression (1) does not correctly represent the phase relation of the two oscillations, as we see by comparing the photograph Pl. XIII. fig. 13, with the calculated curve fig. 6.

*Case VII.* The primary capacity was further reduced, its value in this case being 2.933 microfarads. Taking the other constants as before, we have

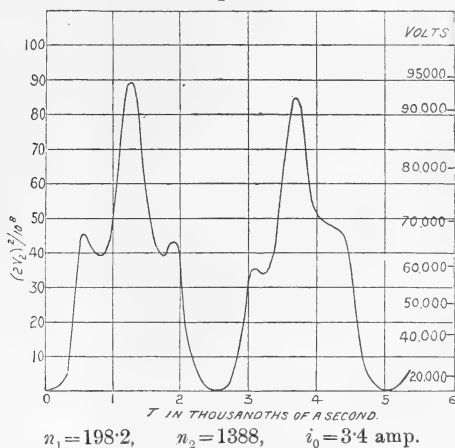
$$n_1 = 198.2, \quad n_2 = 1388,$$

and the expression for the secondary voltage is

$$2V_2 = 24730 i_0 e^{-3.975t} \sin(71359t - 0.12) \\ - 3530 i_0 e^{-65.42t} \sin(499860t - 0.83).$$

The curve, calculated for  $i_0 = 3.4$  amperes, is shown in fig. 7.

Fig. 7.



The photograph shown in Plate XIII. fig. 14 is typical of the oscillograph curves obtained in this case. It again differs from the calculated curve in the relative phases of the two oscillations, and this probably accounts in part for the differences between the observed and calculated maximum voltages given in Table II.

TABLE II.

$i_0$ , amperes.	Maximum Potential in volts.	
	Calc.	Obs.
2.74	75630	70440
3.24	89430	76950
4.00	110400	101100
4.42	122000	112100
5.10	140800	142400

With the current 5.1 amperes the greatest sparking-distance between the two spheres was found to be 11.2 centimetres.

To sum up, the results given above show that the expression (1) represents in its main features the wave of potential at the terminals of the secondary coil when a current is interrupted in the primary, and that it also gives the order of magnitude of the maximum secondary potential. In each of the cases described above some uncertainty with regard to the maximum potential arises from the fact that the amplitude of the oscillograph curve is not always the same with the same primary current; and although each curve was photographed a number of times and the curve of greatest amplitude selected for measurement, we could never be quite certain that the greatest possible amplitude was actually obtained.

Similar differences are observed with other kinds of interrupter. In Plate XIII. fig. 15, are shown the curves of secondary potential at two successive interruptions of the primary current produced by a motor mercury-interrupter of the centrifugal type. The coils and condenser in action at the time were the same as in Case VII.

Bangor, July 1911.

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LXIX. *On the Spectra of the Electrodeless Ring Discharge in certain Gases.* By H. DONALDSON, B.A. (Camb.), B.Sc. (Lond.), Scholar of Sidney Sussex College, Cambridge\*.

IN an ordinary discharge tube with electrodes, the interpretation of the differences in the spectra of a gas in different parts of the tube is rendered difficult by the separation which takes place between the positive and negative ions.

It was thought, therefore, that a study of the spectra of gases in the oscillatory ring discharge, in which a permanent separation between the ions would be unlikely, might afford useful information concerning the dependence of the spectra upon the strength of the ionizing field.

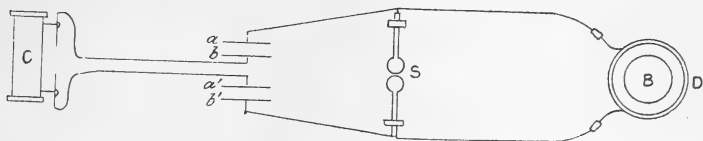
#### *Apparatus.*

The bulbs in which the discharge was obtained were usually about 8 cm. in diameter and were surrounded by a coil of half a dozen turns of well insulated wire wound closely so that the depth of the coil was about 2 cm. The plane through the centre of the coil parallel to the windings was also a

\* Communicated by Professor Sir J. J. Thomson.



diametral plane of the bulb and was vertical. The method of getting the oscillatory discharge in this coil is shown in the diagram.



$a, b, a', b'$ , are the terminals of two leyden-jars,  $a', b$  being connected to the secondary of a Cox induction-coil, and  $a, b'$ , to an adjustable spark-gap  $S$ . To this spark-gap were connected also the terminals of the coil  $D$ , which was placed round the discharge-bulb  $B$  in the manner described. Variations in the intensity of the discharge through  $D$  were obtained by altering the frequency of the hammer-break of the induction-coil, the length of the spark-gap, and the size of the leyden-jars. In the experiments the spark-gap varied between 2 and 15 mm., and the leyden-jars were usually two gallon jars.

The exhaustion of the bulb and the apparatus was carried out by a Toepler mercury pump, and then by charcoal and liquid air, exhaustion to a pressure below that at which any discharge would pass being obtained in each case before the admission of the gas to be examined.

The observing spectroscope was a Hilger constant-deviation instrument in which the wave-lengths of the lines observed could be read directly from a graduated revolving drum. In all cases the gases admitted to  $B$  had been dried by passing through, and being left for some time in contact with, one tube of calcium chloride and two tubes of phosphorus pentoxide, each about 50 cm. long.

### *Method of Experiment*

When the discharge-bulb had been exhausted as above some of the gas to be examined was admitted to the apparatus, which was then gradually exhausted by liquid air and charcoal until the highest pressure at which the true ring discharge would pass was reached. If the spectrum of the discharge gave no indication of the presence of elements other than those composing the gas under observation, the pressure of the gas in the bulb was lowered gradually until no discharge could be obtained, and the spectrum observed at the different stages of this exhaustion. This process was then

repeated, and the effect of variation in the length of the spark-gap and the frequency of sparking was studied.

In all cases, at pressures considerably above the highest at which the ring discharge took place, a feeble electrostatic discharge was seen in the bulb, due to the windings of the surrounding coil not being all in one plane, but this was never used in observations of the spectra.

### *Results.*

*Residual Air*:—The apparatus was washed out several times with air before exhaustion. The spectrum of the discharge was chiefly the positive band spectrum of nitrogen at the highest pressures at which the true ring discharge was obtained, and the colour of the ring was red. At lower pressures many of the nitrogen lines appeared and became very bright as the lower limit of pressure was reached. The negative band spectrum never came out distinctly, even if it were present at all.

Air in which phosphorus had been burned to remove oxygen was then tried and gave the same spectra, a spiral immersed in liquid air being inserted between the inlet apparatus and the bulb to remove the phosphorus and mercury vapours.

Both with residual air and with this deoxygenized air there was an orange after-glow, which persisted brightly for about half a minute after the electric field was removed, and faintly for a much longer time. This afterglow was observed down a tube about a metre long in line with the collimator of the spectroscope. While the discharge was still running the same orange colour could be seen in the centre of the bulb, and its spectrum was continuous throughout the yellow-blue region, but had two places of maximum intensity. As soon as the discharge was cut off, the continuous part of the spectrum died out, but the regions of maximum intensity remained as the spectrum of the true after-glow, in the form of two bands, diffuse on either side and having their centres approximately at wave-lengths 5760 and 5378 tenth-metres, and having a breadth of about 10 such units.

As the first occasion on which this afterglow was observed was one on which there was a possibility of the presence of phosphorus vapour, an entirely new apparatus was set up, but the spectrum remained unchanged.

*Hydrogen*:—The gas was prepared by the action of pure dilute sulphuric acid, to which a trace of copper sulphate solution had been added, upon pure metallic zinc. In the outer of the two rings which constituted the discharge, all

four hydrogen lines appeared at every electric intensity that could be used, though at the highest pressures for the discharge the secondary spectrum was also quite bright. In the inner ring at the pressure for the best discharge, using a short spark, only  $H_\beta$  and  $H_\gamma$  were present. On increasing the spark length  $H_\alpha$  and  $H_\delta$  appeared and became brighter as the spark was still further increased. This association of  $H_\alpha$  with  $H_\delta$  and  $H_\beta$  with  $H_\gamma$  had been observed previously on several occasions with preliminary residual air-bulbs, but in those cases it was always  $H_\alpha$  and  $H_\delta$  which appeared with the shorter spark gap.

*Carbon dioxide*:—The gas was prepared by the action between a solution of pure sodium carbonate and pure dilute sulphuric acid. As in almost every gas, the discharge at the highest pressures was always reddish in colour, probably owing to the presence of a trace of water vapour, but the true colour of the carbon dioxide discharge was dark blue, changing to whitish blue as the pressure decreased, or as the spark-gap and frequency of sparking increased.

The spectrum observed was, in every case, the carbon band spectrum although all possible variations of electric intensity, by varying spark-length, spark frequency, and size of leyden-jars were tried.

*Carbon monoxide*:—The gas was prepared by the action between pure strong formic and sulphuric acids, and on its way to the discharge bulb passed through a spiral tube immersed in liquid air, to remove such impurities as mercury vapour.

Until the apparatus had been washed out some few times with carbon monoxide, the spectrum observed was always the carbon band spectrum. When the carbon monoxide was more pure, the spectrum of the discharge, when a small spark-gap and small leyden-jars were used, was still the carbon band spectrum, but as the spark-length was increased to about 4 mm. the Swan spectrum began to appear and grew in brightness relative to the carbon band spectrum as the spark was still further lengthened. The appearance or disappearance of the Swan bands could be obtained by altering the spark-gap about 1 mm. at the critical length.

At lower pressures, the Swan bands were obtained without so great a lengthening of the spark-gap. The spectrum was the same when large jars were used, but in this case the spark-length could not be made so great and the Swan bands were never quite so bright as with the smaller jars.

*Oxygen*.—The gas was prepared by heating pure potassium

permanganate, and was left in contact with solid potash for some time before it was admitted to the apparatus. The bulb in which the discharge was secured was first exhausted and then washed out six times with oxygen, exhaustion to a pressure below that at which any discharge would pass being carried out after each washing. When the pressure of the gas in the bulb was just low enough for the true ring discharge to pass, the colour of the ring was brick-red, especially on the inner edge, and the spectrum seen was the compound line spectrum. On reducing the pressure, a fairly bright continuous spectrum appeared in the blue, superposed on the compound line spectrum, and this further developed into bright oxygen bands, those having their centres at wave-lengths 5590 and 5245 being especially distinct.

At a still lower pressure, the bright lines of the elementary line spectrum began to flash out brightly at certain instants when the discharge was running well, and ultimately they became steadily bright while the intensity of the bands decreased. The violet lines of the elementary line spectrum were especially bright. The only line which persisted throughout the whole range of pressures was the red (6157).

An attempt was made to produce the changes in the spectra at a medium pressure merely by varying the spark-gap and the frequency of sparking. By increasing these, it was found that the elementary line spectrum appeared at a higher pressure than that at which it appeared with smaller spark-gap and frequency. The band spectrum remained in this case with the larger spark-gap, but rather more faintly.

*Argon* :—Certain colour changes occurring in the ring discharge in argon have already been obtained and described \* and an attempt was made to repeat those observations and to examine the colour changes spectroscopically. The argon first used contained a small percentage of nitrogen which appeared in the spectrum of the light from the inner part of the bulb during the discharge.

At no pressure could any trace of the red argon spectrum be seen, but the blue spectrum was very bright, about 30 lines being measured. A portion of the argon, mixed with pure oxygen, was then sparked for three hours over potash. The excess of oxygen was removed by phosphorus, and the argon remaining was used for the discharge, after the bulb had been washed out several times with it. In this case, at the highest pressures, the ring was red and of the 12 lines measured every one belonged to the red argon spectrum. At an intermediate pressure the number of bright lines

\* Strutt, *Phil. Mag.* xlix. p. 293 (1900).

increased and about 50 were measured, distributed amongst the red and the blue spectra. At the lowest pressures, all the lines belonged to the blue spectrum, but there was practically nothing to be seen in the region between wave-lengths 5879 and 5144. An afterglow having the same orange colour, and giving the same spectrum as the afterglow described in the case of air, was observed in this purified argon at all pressures except the higher and lower limits.

In addition to the above gases were tried hydrochloric and hydrobromic acids, sulphur dioxide, and carbon disulphide. In the case of hydrochloric acid at medium pressures the ring was bluish on the outer edge and reddish on the inner, the difference in colour being due, apparently, to the presence of the hydrogen secondary spectrum in the inner part of the ring. At low pressures the red colour disappeared and the blue extended nearly to the centre of the bulb. The spectrum of the blue part of the ring was the four-line spectrum of hydrogen and the chlorine line spectrum. Hydrobromic acid behaved in a similar manner. The sulphur compounds always gave the sulphur line spectrum and never the band spectrum. In the case of carbon disulphide, the bulb was coated inside with a deposit of sulphur after the discharge had been running. The spectrum of the carbon was the ordinary band spectrum, and not the Swan.

### *Conclusion.*

These experiments clearly indicate a dependence of the spectrum of a gas on the electric field responsible for ionizing the gas. In most cases the results support those obtained previously from observations of the discharge spectra of gases in tubes with metal electrodes\*. In such tubes the intensity of the electric field has been shown to be greater round the cathode than in the positive column, and should also be greater in the intermittent spark discharge with a leyden-jar in circuit than in the continuous discharge. Now in the case of oxygen, the presence of four different emission spectra under different conditions has been shown†; the elementary line spectrum in the leyden-jar discharge, the band spectrum in the negative glow of the continuous discharge, the positive line spectrum in the positive column in a narrow tube, and the continuous spectrum in a wide tube with a weak discharge. In the ring discharge the elementary line spectrum is characteristic of the discharge at

\* Stead, Proc. Roy. Soc. lxxxv. (1911).

† Schuster, Phil. Trans. clxx. p. 37 (1879), and others.

the highest electric intensities used, the band spectrum at intermediate intensities, and the compound line spectrum at the lowest intensities. The only possible difference between the results obtained by the two methods is connected with the continuous spectrum, which in the discharge tube appears at the lowest intensities and in the ring discharge at an intensity between those for the compound line and the band spectra. As considerable doubt has been cast upon the existence of a continuous spectrum in pure oxygen in a discharge tube \*, it is probable that the one observed in the ring discharge is independent of that in the tube discharge. The existence of a band spectrum occupying a position intermediate between two line spectra of the same element is interesting in view of suggestions that have been made to ascribe line spectra to atomic, and band spectra to molecular, systems.

Another case which is interesting from the point of view of the ring discharge is that of the Swan spectrum and the carbon band spectrum. The Swan spectrum only appears in carbon monoxide when it is very nearly pure, and then at a high intensity, and we may have the same bulb showing the carbon band spectrum at a low intensity and the same, mixed with the Swan spectrum, at a higher intensity. As, under the influence of the discharge, carbon dioxide would dissociate into carbon monoxide and oxygen, it would obviously be very difficult in this case to get a sufficient electric intensity in the carbon monoxide itself to cause the appearance of the Swan spectrum. This would also be the case with any impure carbon monoxide, and therefore it would seem possible that the carbon band spectrum and the Swan spectrum may be the low and high intensity spectra of the same substance, though these experiments afford no clue as to whether that substance is carbon monoxide, or carbon in some other form.

In the cases of nitrogen and residual air the ring discharge is peculiar in that it has never shown any clear evidence of the presence of the negative band spectrum, the variation from the positive band spectrum to the line spectrum taking place directly. A bulb containing cyanogen, which was not sufficiently pure to give its own band spectrum, showed a change from the positive to the negative nitrogen band spectrum with increasing electric intensity, but this was never observed in nitrogen itself. The general results agree with those given by discharge tubes in assigning the positive band spectrum in nitrogen to the weakest ionizing fields, and

\* Baly, 'Spectroscopy,' p. 443.

the line spectrum to the strongest, between them being the negative band spectrum.

The ring discharge would appear to be a somewhat powerful method of examining the spectra of slightly impure, or of mixed, gases; as in several cases, particularly those of argon and oxygen, the characteristic spectra of the elements have appeared at stages of purity at which they would have been quite absent in the ordinary vacuum-tube discharge.

In view of the influence of electric intensity on spectra, it would be interesting to study by this method the spectra given by a gas having multiple spectra, when that gas is mixed with traces of different impurities.

In conclusion, I wish most heartily to thank Professor Sir J. J. Thomson for the suggestion at which these experiments were begun, and for his kindly interest and advice throughout their progress.

Cavendish Laboratory, Cambridge.

May 8, 1911.

## LXX. *On the Separation of Spectra in Compound Gases.*

By G. STEAD, B.A., formerly Scholar of Ulster College, Cambridge\*.

**I**N a previous paper† I have described some experiments in which evidence was obtained that a process somewhat akin to electrolysis can occur in gases at low pressure. Compound gases or vapours through which an electric discharge is passed at a pressure of the order of a millimetre usually show the spectra of certain constituents better developed at the anode, whilst the spectra of other components appear more brightly at the cathode. Moreover elements which show a preference for the anode are such as must be supposed on chemical grounds to carry a negative charge, and *vice versa*. Thus in the case of hydrogen chloride the hydrogen spectrum is seen chiefly at the cathode and chlorine lines mainly at the anode. This is partly analogous to what occurs in the electrolysis of a solution of concentrated hydrochloric acid. The present paper gives an account of further work on the same subject, and for a description of the apparatus and method of manipulation the former paper must be consulted.

(i.) *Ethane*.—The gas was prepared pure by the action of distilled water on zinc ethyl.

\* Communicated by the Author.

† Proc. Roy. Soc., August 1911.

When the coil was first turned on the Swan spectrum was seen at both poles, but after a few seconds it was replaced at the anode by carbonic oxide bands, and at the cathode by the "four-line" spectrum of hydrogen. There was no trace of the latter at the positive pole, but there were faint indications of the carbonic oxide spectrum at the negative electrode.

(ii.) *Ethylene Dichloride*.—Initially the Swan spectrum was visible at both electrodes, but in a short time chlorine lines and the ordinary hydrogen spectrum appeared at the cathode, whilst carbonic oxide bands together with a faint secondary hydrogen spectrum were seen at the anode. Carbon was gradually deposited on the walls of the tube.

(iii.) *Ethylidene Dichloride*.—The behaviour of this vapour was precisely analogous to that of ethylene dichloride. Thus there is no difference spectroscopically to be observed between these two isomerides.

(iv.) *Carbonyl Chloride (phosgene gas)*.—At the anode bright carbonic oxide bands were observed, whilst chlorine lines showed brilliantly at the cathode. The separation of the two spectra in this case was practically complete. There was no deposition of carbon on the walls of the tube.

(v.) *Mercury Dimethyl*.—Liquid air was used to freeze out any mercury vapour which might come over from the Töpler pump. The liquid was admitted into an exhausted bulb through a tap in the usual way (see previous paper), except that mercury could not be used here to displace the air from the bore of the tap. This air was therefore removed by running a little of the mercury dimethyl itself through the tap, the bulb being then re-exhausted by means of charcoal and liquid air.

At first when the discharge was passed the mercury lines (5791, 5769, 5461, 4358) appeared very brilliantly at both poles, and they were accompanied on the positive side only by a pure Swan spectrum, *i. e.* pure in that there was no trace of the carbonic oxide spectrum. No hydrogen lines were seen until the coil had been running some seconds, when they appeared chiefly at the cathode. After a short time the pressure diminished, and carbonic oxide bands became visible at both electrodes. The greater the initial pressure the longer it took before the spectrum of carbonic oxide was seen. Finally a condition was reached in which hydrogen showed mainly at the cathode, and carbonic oxide principally at the anode, whilst mercury lines were visible faintly at both electrodes.

(vi.) *Aniline*.—At the cathode the four-line spectrum of



hydrogen was very brilliant, and was accompanied by somewhat faint negative bands of nitrogen. At first the Swan spectrum was seen for a few seconds at the anode, but it was rapidly replaced by carbonic oxide. There were also very faint traces of a number of bands in the violet, most probably constituting part of the positive pole spectrum of nitrogen. There appeared to be no tendency to deposit carbon on the walls of the discharge-tube.

Thus it seems as though the electropositive amido-group had a tendency to go to the cathode, and the benzene nucleus to the anode. This would explain the presence of the spectra of hydrogen and nitrogen at the negative pole, and of carbonic oxide at the positive pole.

(vii.) *Ethyl Ether*.—When the coil was first turned on the Swan spectrum was bright and the carbonic oxide spectrum faint at the positive pole, whilst at the cathode the converse was true. After a few seconds the Swan spectrum at the anode was replaced by carbonic oxide bands, whilst at the cathode the ordinary spectrum of hydrogen became visible. No carbon was deposited on the walls of the tube, but, in spite of this, decomposition apparently took place, for the passage of the discharge caused a considerable permanent rise of pressure.

(viii.) *Methyl Sulphide*.—Initially both poles showed Swan bands, but these were rapidly replaced at the cathode by carbonic oxide and the four-line spectrum of hydrogen. Later on sulphur bands appeared at the anode, and after remaining fairly bright for some minutes at length gave place to the carbonic oxide spectrum. Decomposition took place fairly readily and carbon was deposited on the sides of the tube. Thus in methyl sulphide sulphur shows a preference for the anode just as in the case of hydrogen sulphide and carbon disulphide.

(ix.) *Chloroform Vapour in a very short tube*.—A tube was used in which the electrodes were only about 1.5 cm. apart. With pressures of the order of 0.5 cm. and a weak discharge perfectly normal results were obtained. When, however, the pressure was taken down to about half a millimetre, and a heavy discharge was sent through the tube, the discharge became completely oscillatory, in spite of the "point and plane" spark-gap in use. The anode and cathode could be distinguished no longer, whilst the positive column practically disappeared. In these circumstances chlorine lines appeared throughout the tube, and very little could be seen of the carbonic oxide bands which are normally present in the positive column.

*General Remarks.*—In my previous paper (*loc. cit.*) I have shown that, when a discharge is passed through hydrogen chloride, the chlorine spectrum appears at the anode, whereas in chloroform, chlorobenzene, stannic chloride, &c., it is found chiefly at the cathode. I have also pointed out that chemical considerations indicate very conclusively that the chlorine in hydrogen chloride carries a negative charge, but that in the other substances referred to it carries a positive charge. The results of the work described in the present paper show that the chlorides of ethylene and ethylidene, and likewise phosgene gas, behave in a manner analogous to that of chloroform &c. Thus it would seem very probable that the sign of the charge carried by the atoms is of fundamental importance in connexion with the separation of spectra in a discharge-tube.

At the same time it appears impossible to regard this as the only cause of the differences in the spectra at the anode and cathode, since such differences are often found in an elementary gas. Thus in oxygen the negative pole shows a band spectrum and the positive pole a line spectrum; in nitrogen the band spectra at the two electrodes are altogether different, whilst in hydrogen I have found perfectly definite differences. Professor Sir J. J. Thomson also showed a good many years ago that the spectra of this gas at the two electrodes are not identical. The anode favours the production of the secondary spectrum of hydrogen, and is particularly unfavourable to the blue line  $H\beta$  (4861) of the ordinary spectrum. The four-line spectrum is well developed at the cathode, the blue line being here especially bright. Now we can scarcely regard the blue line as being due to positively charged hydrogen atoms and the red line  $H\alpha$  (6563) to negatively charged hydrogen atoms, because these lines both belong to the same spectral series, and therefore must be presumed to have the same origin. Hence the differences in hydrogen can be hardly assigned to electrochemical effects.

Now it is known that the secondary hydrogen spectrum is favoured by a weak discharge and the primary spectrum by a strong discharge. Again, in oxygen the negative band spectrum has been obtained away from the negative pole, indeed in the absence of any poles at all. Thus Donaldson\* got it with the electrodeless ring-discharge at an intensity intermediate between that required for the compound line spectrum and that necessary to produce the elementary line spectrum. It seems therefore that the intensity of the

\* Vide *suprà*, p. 724.

discharge is a most important factor. Now small intensity implies low (electrical) temperature; and it is known that the effective temperature of the anode is much less than that of the cathode. Therefore it appears likely that there are at least two causes of the differences between the anode and cathode spectra of gases, viz.:—

(a) The inequality of temperature (and potential gradient) at the two electrodes.

(b) The electrochemical character of the elements concerned.

Kayser, in his great *Handbuch der Spectroscopie*, somewhat boldly asserts that (a) alone is effective\*. He is led to this conclusion, apparently, by an experiment of Morris-Airey's† which seems to be antagonistic to (b). A discharge was passed for some time through a tube containing hydrogen and a little chlorine. The tube was then divided into two portions, and the chlorine spectrum was found to show the same intensity at the anode of each half tube. It is claimed that this proves there is no appreciable separation of hydrogen and chlorine by a process of the nature of electrolysis. But this conclusion does not appear to me to be justifiable. Might it not be almost as well said that, because in the electrolysis of dilute sulphuric acid bubbles of oxygen can be *seen* only at the anode, therefore no oxygen exists anywhere else in the voltameter? Just as oxygen may be present in the liquid without being detected by eye, so may the chlorine be distributed throughout the tube, and yet not show its spectrum except where its ions are being discharged, viz. at the anode. Further, even granting that this experiment does prove the absence of a process resembling liquid electrolysis, it is still far from legitimate to assume that (a) is the only cause, for the scope of (b) is not by any means limited to pure electrolysis (*i. e.* a process subject to Faraday's laws).

That (a) alone is quite incapable of explaining the facts seems perfectly clear. Otherwise how is it that in no case has an electronegative element been found spectroscopically only at the cathode, or an electropositive one only at the anode? Why should electronegative elements in nearly every case show a preference for the positive pole, and electropositive elements for the negative pole? When a substance which, like chlorine, is normally electronegative is known from chemical evidence to be acting as an electropositive element, it is seen by the spectroscope at the cathode instead of as usual at the anode. If appreciable separation occurs at

\* Kayser, *Handbuch der Spectroscopie*, vol. ii. pp. 174, 175.

† Morris-Airey, *Drude Ann.* i. 1900, p. 466; also *Phil. Mag.* [5] xlix. p. 307 (1900).

all, elements always go to the pole that is of opposite sign to the charge which chemical considerations indicate they carry. Were Kayser's view of the matter correct, all these curious facts, so far from being explained, must be supposed to be merely the result of chance. Moreover, there would appear to be a fatal objection to the view that the differences in the spectra at the two electrodes are to be ascribed solely to temperature differences. Take the case of carbon disulphide. With the hammer-break no sulphur bands are seen at all; and this is true also for the Wehnelt interrupter so long as the current is kept small. But as the temperature is gradually raised by increasing the current, the band spectrum of sulphur appears *at the anode*. Now if this be a pure temperature effect, why do not the sulphur bands show first at the cathode, since the latter is always hotter than the anode? This objection (if valid) also disposes of Kayser's explanation of the lingering of spectra when the coil is reversed (see previous paper), viz. that as the temperature at the electrodes cannot change suddenly, the spectra cannot do so either. A similar argument is afforded by hydrogen sulphide. Hence the hypothesis (*a*) can hardly be regarded as otherwise than inadequate; in other words, some further explanation is necessary. For this, I believe that (*b*) in the main suffices. It is not asserted that there are no difficulties connected with (*b*); it is claimed that (*a*) is insufficient, and that (*b*) is in some way involved.

To give a perfectly satisfactory and complete explanation is a matter of extreme difficulty, and indeed is probably an impossibility in the present state of our knowledge. It is not known with any certainty what are the processes involved in the production of spectra, and there are many questions to be answered in connexion with the structure of a vacuum-tube discharge. Why is there a definite positive column? What is the meaning of the negative glow? Why do certain parts of the tube give out little or no light (Faraday's and Crookes's dark spaces). So long as there is any doubt about these points we cannot account in detail for the phenomena described in this paper.

In framing any explanatory hypothesis certain points must be borne in mind:—

(1) There is a kind of electrolysis or pseudo-electrolysis taking place.

(2) The intensity of the discharge is of fundamental importance, probably because high intensity is associated with

high temperature. The effective temperature at the cathode is higher than the effective temperature at the anode.

(3) In general (though not always) the cathode spectrum is seen throughout the negative glow, whilst the anode spectrum is found all along the positive column.

(4) The current can be carried through the tube independently of ordinary matter, viz. by corpuscles; and hence pure electrolysis is impossible. We cannot expect to find Faraday's laws obeyed.

It is perhaps legitimate to go so far as to say that in all probability positive ions move under the influence of the electric force towards the cathode, and negative ions towards the anode, as in the case of liquid electrolysis. If the usual theory of the production of spectra be accepted (*i. e.* that the essence of the process is the discharge of ions), it must be supposed that the discharge of positive ions takes place throughout the negative glow, whilst negative ions lose their charges in the positive column. If we then consider the process to be analogous to electrolysis of solutions, we must regard the whole negative glow as constituting the cathode, and the positive column as equivalent to the anode.

#### *Summary.*

It has been found that when an electric discharge is passed through a gas at low pressures the spectrum of the glow around the cathode differs from that of the light from the neighbourhood of the anode. In compound gases the spectra which appear at the cathode are due to atoms which, from chemical considerations, must be supposed to carry a positive charge. Similar remarks apply to the anode. It is thought that the principal factors which determine the differences in the spectra at the two electrodes are:—

(1) The difference in temperature and electric force at the two poles.

(2) The electrochemical character of the elements concerned.

These experiments have been conducted throughout in the Cavendish Laboratory under the direction of Professor Sir J. J. Thomson, whom I take this opportunity to thank for his numerous suggestions and kindly interest in the work.

Cavendish Laboratory, Cambridge.

July 6th, 1911.

LXXI. *On the General Problem of Photographic Reproduction, with suggestions for enhancing Gradation originally invisible.*  
By LORD RAYLEIGH, O.M., F.R.S.\*

IN copying a subject by photography the procedure usually involves two distinct steps. The first yields a so-called *negative*, from which, by the same or another process, a second operation gives the desired *positive*. Since ordinary photography affords pictures in monochrome, the reproduction can be complete only when the original is of the same colour. We may suppose, for simplicity of statement, that the original is itself a transparency, *e. g.* a lantern-slide.

The character of the original is regarded as given by specifying the transparency ( $t$ ) at every point, *i. e.* the ratio of light transmitted to light incident. But here an ambiguity should be noticed. It may be a question of the place at which the transmitted light is observed. When light penetrates a stained glass, or a layer of coloured liquid contained in a tank, the direction of propagation is unaltered. If the incident rays are normal, so also are the rays transmitted. The action of the photographic image, constituted by an imperfectly aggregated deposit, differs somewhat. Rays incident normally are more or less diffused after transmission. The effective transparency in the half-tones of a negative used for contact printing may thus be sensibly greater than when a camera and lens is employed. In the first case all the transmitted light is effective; in the second most of that diffused through a finite angle fails to reach the lens†. In defining  $t$ —the transparency at any place—account must in strictness be taken of the manner in which the picture is to be viewed. There is also another point to be considered. The transparency may not be the same for different kinds of light. We must suppose either that one kind of light only is employed, or else that  $t$  is the same for all the kinds that need to be regarded. The actual values of  $t$  may be supposed to range from 0, representing complete opacity, to 1, representing complete transparency.

As the first step is the production of a negative, the question naturally suggests itself whether we can define the ideal character of such a negative. Attempts have not been wanting; but when we reflect that the negative is only a means to an end, we recognize that no answer can be given without reference to the process in which the negative is to

\* Communicated by the Author.

† In the extreme case a negative seen against a dark background and lighted obliquely from behind may even appear as a positive.

be employed to produce the positive. In practice this process (of printing) is usually different from that by which the negative was itself made; but for simplicity we shall suppose that the same process is employed in both operations. This requirement of identity of procedure in the two cases is to be construed strictly, extending, for example, to duration of development and degree of intensification, if any. Also we shall suppose for the present that the *exposure* is the same. In strictness this should be understood to require that both the intensity of the incident light and the time of its operation be maintained; but since between wide limits the effect is known to depend only upon the product of these quantities, we may be content to regard exposure as defined by a single quantity, viz. *intensity of light*  $\times$  *time*.

Under these restrictions the transparency  $t'$  at any point of the negative is a definite function of the transparency  $t$  at the corresponding point of the original, so that we may write

$$t' = f(t), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$f$  depending upon the photographic procedure and being usually such that as  $t$  increases from 0 to 1,  $t'$  decreases continually. When the operation is repeated upon the negative, the transparency  $t''$  at the corresponding part of the positive is given by

$$t'' = f(t'), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Complete reproduction may be considered to demand that at every point  $t'' = t$ . Equation (2) then expresses that  $t$  must be the same function of  $t'$  that  $t'$  is of  $t$ . Or, if the relation between  $t$  and  $t'$  be written in the form

$$F(t, t') = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$F$  must be a *symmetrical* function of the two variables. If we regard  $t, t'$  as the rectangular coordinates of a point, (3) expresses the relationship by a *curve* which is to be symmetrical with respect to the bisecting line  $t' = t$ .

So far no particular form of  $f$ , or  $F$ , is demanded; no particular kind of negative is indicated as ideal. But certain simple cases call for notice. Among these is

$$t + t' = 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which obviously satisfies the condition of symmetry. The representative curve is a straight line, equally inclined to the axes. According to (4), when  $t = 0, t' = 1$ . This requirement is usually satisfied in photography, being known as freedom

from fog—no photographic action where no light has fallen. But the complementary relation  $t'=0$  when  $t=1$  is only satisfied approximately. The relation between negative and positive expressed in (4) admits of simple illustration. If both be projected upon a screen from independent lanterns of equal luminous intensity, so that the images fit, the pictures obliterate one another, and there results a field of uniform intensity.

Another simple form, giving the same limiting values as (4), is

$$t^2 + t'^2 = 1; \dots \dots \dots (5)$$

and of course any number of others may be suggested.

According to Fechner's law, which represents the facts fairly well, the visibility of the difference between  $t$  and  $t+dt$  is proportional to  $dt/t$ . The gradation in the negative, constituted in agreement with (4), is thus quite different from that of the positive. When  $t$  is small, large differences in the positive may be invisible in the negative, and *vice versa* when  $t$  approaches unity. And the want of correspondence in gradation is aggravated if we substitute (5) for (4). All this is of course consistent with complete final reproduction, the differences which are magnified in the first operation being correspondingly attenuated in the second.

If we impose the condition that the gradation in the negative shall agree with that in the positive, we have

$$dt/t = -dt'/t', \dots \dots \dots (6)$$

whence

$$t.t' = C, \dots \dots \dots (7)$$

where  $C$  is a constant. This relation does not fully meet the other requirements of the case. Since  $t'$  cannot exceed unity,  $t$  cannot be less than  $C$ . However, by taking  $C$  small enough, a sufficient approximation may be attained. It will be remarked that according to (7) the negative and positive obliterate one another when superposed in such a manner that light passes through them in succession—a combination of course entirely different from that considered in connexion with (4). This equality of gradation (within certain limits) may perhaps be considered a claim for (7) to represent the ideal negative; on the other hand, the *word* accords better with definition (4).

It will be remembered that hitherto we have assumed the exposure to be the same in the two operations, viz. in producing the negative and in copying from it. The restriction is somewhat arbitrary, and it is natural to inquire whether it



can be removed. One might suppose that the removal would allow a greater latitude in the relationship between  $t$  and  $t'$ ; but a closer scrutiny seems to show that this is not the case.

The effect of varying the exposure ( $e$ ) is the same as of an inverse alteration in the transparency; it is the product  $et$  with which we really have to do. This refers to the first operation; in the second,  $t''$  is dependent in like manner upon  $e't'$ . For simplicity and without loss of generality we may suppose that  $e=1$ ; also that  $e'/e=m$ , where  $m$  is a numerical quantity greater or less than unity. The equations which replace (1) and (2) are now

$$t'=f(t), \quad t=t''=f(mt'); \quad . \quad . \quad . \quad . \quad (8)$$

and we assume that  $f$  is such that it decreases continually as its argument increases. This excludes what is called in photography *solarization*.

We observe that if  $t$ , lying between 0 and 1, anywhere makes  $t'=t$ , then  $m$  must be taken to be unity. For in the case supposed

$$t=f(t)=f(mt);$$

and this in accordance with the assumed character of  $f$  cannot be true, unless  $m=1$ . Indeed without analytical formulation it is evident that since the transparency is not altered in the negative, it will require the same exposure to obtain it in the second operation as that by which it was produced in the first. Hence, if anywhere  $t'=t$ , the exposures must be the same.

It remains to show that there is no escape from a local equality of  $t$  and  $t'$ . When  $t=0$ ,  $t'=1$ , or (if there be fog) some smaller positive quantity. As  $t$  increases from 0 to 1,  $t'$  continually decreases, and must therefore pass  $t$  at some point of the range. We conclude that complete reproduction requires  $m=1$ , *i. e.* that the two exposures be equal; but we must not forget that we have assumed the photographic procedure to be exactly the same, except as regards exposure.

Another reservation requires a moment's consideration. We have interpreted complete reproduction to demand equality of  $t''$  and  $t$ . This seems to be in accord with usage; but it might be argued that *proportionality* of  $t''$  and  $t'$  is all that is really required. For although the pictures considered in themselves differ, the effect upon the eye, or upon a photographic plate, may be made identical, all that is needed being a suitable variation in the intensity of the luminous background. But at this rate we should have to regard a white and a grey paper as equivalent.

If we abandon the restriction that the photographic process is to be the same in the two operations, simple conclusions of generality can hardly be looked for. But the problem is easily formulated. We may write

$$t' = f_1(et), \quad t = t'' = f_2(e't'), \quad . \quad . \quad . \quad (9)$$

where  $e, e'$  are the exposures, not generally equal, and  $f_1, f_2$  represent two functions, whose forms may vary further with details of development and intensification. But for some printing processes  $f_2$  might be treated as a fixed function. It would seem that this is the end at which discussion should begin. When the printing process is laid down and the character of the results yielded thereby are determined, it becomes possible to say what is required in the negative; but it is not possible before.

In many photographs it would appear that gradation tends to be lost at the ends of the scale, that is in the high lights and deep shadows, and (as a necessary consequence, if the full range is preserved) to be exaggerated in the half-tones. For some purposes, where precise reproduction is not desired, this feature may be of advantage. Consider, for example, the experimental problem, discussed by Huggins, of photographing the solar corona without an eclipse. The corona is always present, but is overpowered by atmospheric glare. The problem is to render evident a very small relative difference of luminous intensity. If the difference is exaggerated in a suitably exposed and developed photograph, so much the better. A repetition of successive copyings might render conspicuous a difference originally invisible. At each operation we may suppose a factor  $a$  to be introduced,  $a$  being greater than unity. After  $n$  copyings  $dt/t$  becomes  $a^n dt/t$ . Unless the gain each time were very decided, this would be a slow process, and it would be liable to fail in practice owing to multiplication of slight irregular photographic markings. But a method proposed by Mach\* and the present writer† should be of service here. By the aid of reflexion light at each stage is transmitted *twice* through the picture. By this means alone  $a$  is raised to equality with 2, and upon it any purely photographic exaggeration of gradation is superposed. Three successive copyings on this plan should ensure at least a ten-fold exaltation of contrast.

\* Eder's *Jahrbuch f. Photographie*.

† Phil. Mag. xliv. p. 282 (1897); Scientific Papers, vol. iv. p. 333.

Another method, simpler in execution, consists in superposing a considerable number ( $n$ ) of similar pictures. In this way the contrast is multiplied  $n$  times. Rays from a small, but powerful, source of light fall first upon a collimating lens, so as to traverse the pile of pictures as a parallel beam. Another condensing lens brings the rays to a focus, at which point the eye is placed. Some trials on this plan made a year ago gave promising results. Ten lantern-slides were prepared from a portrait negative. The exposure (to gas-light) was for about 3 seconds through the negative and for 30 seconds bare, *i. e.* with negative removed, and the development was rather light. On single plates the picture was but just visible. Some rough photometry indicated that each plate transmitted about one-third of the incident light. In carrying out the exposures suitable stops, cemented to the negative, must be provided to guide the lantern-plates into position, and thus to ensure their subsequent exact superposition by simple mechanical means.

When only a few plates are combined, the light of a Welsbach mantle suffices; but, as was to be expected, the utilization of the whole number (ten) requires a more powerful source. Good results were obtained with a lime-light; the portrait, barely visible at all on the single plates, came out fairly well under this illumination. If it were proposed to push the experiment much further by the combination of a larger number of plates, it would probably be advantageous to immerse them in benzole contained in a tank, so as to obviate the numerous reflexions at the surfaces.

It has been mentioned that in the above experiment the development of the plates was rather light. The question may be raised whether further development, or intensification, might not make one plate as good as two or three superposed. I think that to a certain extent this is so. When in a recent experiment one of the plates above described was intensified with mercuric chloride followed by ferrous oxalate, the picture was certainly more apparent than before, when backed by a sufficiently strong light. And the process of intensification may be repeated. But there is another point to be considered. In the illustrative experiment it was convenient to copy all the plates from the same negative. But this procedure would not be the proper one in an attempt to render visible the solar corona. For this purpose a good many independent pictures should be combined, so as to eliminate slight photographic defects. As in many physical measurements, when it is desired to enhance the delicacy,

the aim must be to separate feeble constant effects from chance disturbances.

It may be that, besides that of the corona, there are other astronomical problems to which one or other of the methods above described, or a combination of both, might be applied with a prospect of attaining a further advance.

Aug. 1911.

LXXII. *A Relation between Tension and Torsion.* By R. A. HOUSTOUN, M.A., D.Sc., Ph.D., Lecturer on Physical Optics in the University of Glasgow\*.

IN this Journal ("On Magnetostriction," Phil. Mag. xxi. p. 78, 1911) I recently† gave a simple relation connecting magnetostriction with the change of magnetization produced in a wire by stretching. I desire here to call attention to a similar relation connecting the torsion of a wire with its tension. This relation appears to me to be wholly new.

Suppose that a wire is hanging vertically, its upper end being fixed, and that its lower end is acted on by a stretching force  $F$  vertically downwards and by a couple  $L$ . Let  $x$  be the increase of length and  $\theta$  the angle of twist at the lower end.

If  $U$  denote the intrinsic energy of the wire,

$$\begin{aligned} dU &= F dx + L d\theta \\ &= F \left( \frac{\partial x}{\partial F} dF + \frac{\partial x}{\partial L} dL \right) + L \left( \frac{\partial \theta}{\partial F} dF + \frac{\partial \theta}{\partial L} dL \right) \\ &= \left( F \frac{\partial x}{\partial F} + L \frac{\partial \theta}{\partial F} \right) dF + \left( F \frac{\partial x}{\partial L} + L \frac{\partial \theta}{\partial L} \right) dL. \end{aligned}$$

Since this is a perfect differential,

$$\begin{aligned} \frac{\partial}{\partial L} \left( F \frac{\partial x}{\partial F} + L \frac{\partial \theta}{\partial F} \right) &= \frac{\partial}{\partial F} \left( F \frac{\partial x}{\partial L} + L \frac{\partial \theta}{\partial L} \right) \\ \text{or} \quad \frac{\partial \theta}{\partial F} &= \frac{\partial x}{\partial L}. \end{aligned}$$

This is the new relation referred to.

It also comes very simply from consideration of a cycle.

\* Communicated by the Author.

† In the *Beiblätter* (1911, xxxv. p. 717) Prof. R. Gans states that the former paper is inaccurate inasmuch as the volume is taken independent of stretching force and field strength. But the terms thus introduced can be neglected.

The same cycle is represented in the figure both on the  $Fx$  and  $L\theta$  diagrams, A, B, C, and D corresponding on the one

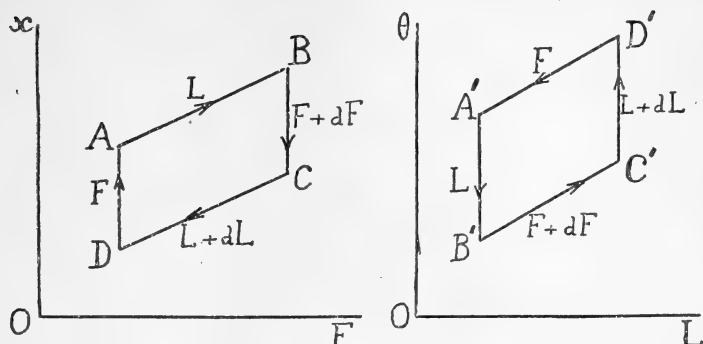


diagram to A', B', C', and D' on the other. The work done in the cycle must be zero. The two parallelograms are traversed in opposite directions; hence their areas must be equal.

$$A B C D = dF \frac{\partial x}{\partial L} dL,$$

and

$$A' B' C' D' = dL \frac{\partial \theta}{\partial F} dF.$$

Therefore, on equating,

$$\frac{\partial \theta}{\partial F} = \frac{\partial x}{\partial L}.$$

There are no measurements available for testing the relation. E. G. Coker (Edin. Trans. xl. p. 263, 1901-02) has tried both the effect of tension on torsion and torsion on tension, but the results are hardly greater than the error of observation.

In any case  $\frac{\partial x}{\partial L}$  would be extremely difficult to determine experimentally.

LXXIII. *On the Origin of Cometary Bodies and Saturn's Rings.* By HENRY WILDE, D.Sc., D.C.L., F.R.S.\*

[Plates XIV. & XV.]

AS the first Halley Lecture which I delivered before the University of Oxford in May last† contained some matters new to astronomical science, it has appeared to me that an abridgment of the lecture, with some additions

\* Communicated by the Author. From the Manchester Memoirs, vol. iv. 1910, no 1.

† Clarendon Press. Frowde. 1910.

which have since presented themselves to me, would be of value in continuation of my papers recently published by the Society\*.

While the principle of dualism is abundantly manifest in every department of knowledge and fully recognized in the attractions and repulsions in molecular physics, the phenomena of the repulsive energy of celestial bodies have so far been unduly obscured by the more general principles of moving force and the attraction of gravitation.

The doctrine that the solar system, as at present constituted, was formed by the successive condensations of a nebular substance rotating about a central position, has been more firmly established during recent years through the great advances made in stellar photography, by which many of the nebulae are visualized in various stages of evolution as right- and left-handed spirals, and clearly indicating the direction of their revolutions†.

The more interesting of these nebulae are M.31 Andromedæ, M.51 Canum, M.100 Comæ, M.74 Piscium, and many others from which the origin of planetary systems may be inferred with the same degree of probability as in the historical sequences observable in chemistry, geology, biology, or in any other department of the natural sciences.

That the subsequent condensations of planetary nebulae into spherical bodies would be attended by the evolution of an amount of heat sufficient to make them vividly incandescent, is an obvious conclusion drawn directly from experimental science. It will be further evident that, after the heat of compression had attained its maximum, the self-luminous planets would ultimately become dark bodies through the radiation of their heat into free space.

It is very generally admitted that the sun, notwithstanding his vast dimensions, would, by continuous loss of heat, ultimately become a dark body like each member of the planetary system. It is also known that the internal parts of the sun are in a gaseous condition and under immense pressure. Some idea of the repulsive force exercised by this pressure may be formed from the ejection of enormous masses of incandescent gas from the surface of the sun to the height of 200,000 miles, with an estimated velocity of 166 miles per second‡.

\* Manchester Memoirs, vols. liii. liv. 1909, 1910. Phil. Mag. [6] vols. xviii. xix. 1909, 1910.

† "Celestial Photographs," by Isaac Roberts, F.R.S., vols. i. ii. 1893, 1899.

‡ Young, American Journal of Science, 1871, p. 468.

Assuming the secular cooling of the sun to be continuous, the liquefaction and final solidification of his outward parts would follow in natural sequence in accordance with common experience of cooling bodies, while the central parts would remain in their primitive gaseous condition. From strict analogy, it may justly be inferred that all the planetary bodies have gone through the same stages of cooling as those outlined in the instance of the central body.

The notion that the earth and, inferentially, the other planets are solid bodies throughout, finds no support from a reasonable consideration of the constituents of the earth's crust, so far as they are accessible to observation. The late distinguished Professor of Geology in Oxford University (Sir Joseph Prestwich), in his classical work on Chemical, Physical, and Stratigraphical Geology, has clearly demonstrated from the uplift of continental areas and mountain chains, the welling out of basaltic lavas over many thousand square miles of surface and of great thickness, that a comparatively thin crust enveloping a fluid interior is a necessary condition to satisfy the requirements of geologists and physicists. More significant still is the succession of foldings of the earth's crust and stratigraphic contortions of small curvature, both of which features indicate a thickness of solid crust less than twenty-five miles. How far the imprisoned gases at the centre of the earth and the aqueous vapours near the surface may have contributed respectively to produce these geological changes, it is unnecessary now to discuss, but in the instance of the moon, which has neither water nor an atmosphere, the evidence of intense volcanic action manifested on its surface can only be accounted for by the ejective force of the gaseous substances in its interior, similar to that by which the incandescent gases from the surface of the sun are projected.

The fine series of photographic enlargements of the moon executed by MM. Loewy and Puiseux, of the Paris Observatory, show the greater part of its surface, from the equator to the poles, covered with extinct volcanoes in every stage of formation, similar to those on the terrestrial globe. Some of these volcanoes are twelve thousand feet in height, with their craters upwards of forty miles in diameter, and are striking evidence of the immense repulsive force which produced them.

It has for a long time been considered on good evidence that the planetoids between the orbits of Mars and Jupiter (now numbering more than 600) are the fragments of a large planet which had formerly revolved in an orbit about the

same distance from the sun as Ceres, and had been shattered by some internal convulsion. This hypothesis was put forward by Olbers the discoverer of Pallas in 1802, and was made the subject of a memoir by Lagrange, in which he determined the explosive force necessary to detach a fragment of a planet that would cause it to describe the orbit of a comet. The nebulosities of the dense atmospheres of some of these planetoids concealing their disks indicate an incipient change of planetary into cometary bodies.

Attempts have been made during recent years to discredit the explanation offered by Olbers of the origin of the planetoids, by assuming that the annulus or convolute of nebular substance failed to resolve itself into a sphere, but was broken up into a number of small bodies.

There is no inherent improbability in the idea of a nebular convolution resolving itself into a number of discrete spherical bodies, as many of such are to be seen in the convolutions of spiral nebulae, of which M. 100 Comæ and M. 74 Piscium are the most striking examples. The convolutions of these nebulae contain nebular stars which are involved symmetrically, and follow the curvature of the convolutions. M. 100 Comæ is further interesting from the fact of its showing elongated fissions of the convolutions previous to their development into spherical bodies. Such discrete bodies, revolving in a circular orbit of the same diameter, would, by their mutual attractions, ultimately coalesce to form a single planet, as postulated in my paper in connexion with the contraction of the radius vector of Neptune\*.

As the orbits of all the planets are nearly in the plane of the ecliptic, and also of comparatively small eccentricity, it would become necessary to further assume that all the rings of discrete bodies should revolve in the same plane of the ecliptic, and in orbits nearly circular as do the other planetary bodies; but Olbers found that Pallas had the large orbital inclination of  $34^{\circ}7'$ , and many others are inclined from 26 to 15 degrees.

The eccentricities of some of the planetoids are also very large, that of *Æthra* being 0.380, *Juno* 0.257, and *Pallas* 0.238. The periodic times vary between 7.86 years (*Hilda*) and 1.75 years (*Eros*) with the correlated large differences in their mean distances from the sun; *Hilda* being 3.95 astronomical units, and *Eros* only 1.46 units, which thereby intersects the orbit of Mars, 1.52 units.

The large differences observable in the elements of the

\* Manchester Memoirs, vol. liv. 1910. Phil. Mag. [6] vol. xix. 1910, p. 604.



planetoids clearly indicate them as fragments of a large planet, in accordance with the conclusions arrived at by Olbers in 1802. The illustrious astronomer further assumed that the orbits of all the fragments would intersect each other at the point where the explosion occurred. Subsequent observations have, however, shown (which I shall confirm further on) that this supposition, while applicable in many instances, does not hold good as a generalization.

It will now be evident, without further discussion, that had the exploded major planet been a solid body throughout as hard as steel, it would still be revolving in its orbit, and would thus have deprived the world of an interesting chapter of astronomical science.

A review of the history of cometary astronomy brings out the remarkable fact that, while much has been written on the nature and motions of comets, few, if any, serious attempts have been made to account for their origin. The general opinion of modern astronomers, in accordance with the views of Kant\* and Laplace†, is that these bodies are strangers to the solar system, which have been captured in the course of their lawless wanderings from the depths of the stellar universe.

The principal objection to this supposition is the immense distance of the solar system from the fixed stars. The best determination of the distance of the nearest of them was made by Dr. Gill at the Cape of Good Hope in 1881, which showed that  $\alpha$  Centauri had a parallax of  $0''.75$ , indicating a distance of about 25 billion miles, or 9000 times more distant from Neptune than that planet is from the sun. As the attraction of gravitation at the orbit of Neptune is only one forty-second millionth of that at the solar surface, the attractive force at the distance of the fixed stars may be considered a negligible quantity in determining the motions of cometary bodies having their origin in other planetary systems. Granting for the moment that comets actually belong to other stellar systems, the problem of their origin and formation would still present itself for solution to earnest inquirers into the nature and causes of things.

The discoveries in cometary astronomy, more especially those of Schiaparelli, that the orbits of certain comets are identical with those of well-known streams of meteors, as instanced in the comets of Tempel and of Biela in relation to the November meteors, clearly point to the conclusion that the place of origin of these erratic bodies is within the

\* Kant's 'Natural History and Theory of the Heavens,' Chapter 3.

† Laplace's *Système du Monde*, 1824.

confines of the solar system, and that they have, consequently, always been members of it. Moreover, all meteoric bodies, as is well known, are mechanical mixtures of elementary substances or their compounds, and further indicate them as the ejectamenta of planetary bodies.

That comets are planetary ejectamenta, principally from the larger planets, may be justly inferred from the prodigious force manifested by the ejections from other celestial bodies to which attention has already been directed.

The determining cause of the ejection of a comet from any planet would be found in the conjunctive attractions of one or more of their number acting upon that part of the surface from which the cometary matter was ejected. The orbital direction of a comet would be determined solely by the position of the breach in the crust in relation to the orbital motion at the moment of discharge. The motion would be *direct* when its discharge coincided with the orbital motion of the planet, and *retrograde* when it was in the opposite direction, as shown in the annexed plate (Pl. XIV. fig. 1). And, according as the discharge was more or less at right angles to the plane of the planetary orbit, so would the angular direction of the comet in relation to the ecliptic be determined. The discharge of cometary bodies from vents in high planetary latitudes would necessarily have the greatest inclination to the ecliptic. It may be observed in this connexion that some of the large craters on the moon's surface, and of the terrestrial active volcanoes, Hecla and Mount Erebus, are also in high latitudes.

To those who are not familiar with the problems of experimental mechanics, it may be of some advantage to demonstrate more fully the direct and retrograde motions of cometary bodies by further illustrations than those shown in my Halley lecture.

It is common knowledge, based on well-established observations, that the axial and orbital rotations of all the planets are in the same direction, the sun also revolving on its axis in the same direction as the planets.

As a consequence of the common direction of the axial rotations, the circumferential parts revolve in opposite directions to each other, as will be seen in the annexed diagram of the sun and Jupiter (Pl. XIV. fig. 1). Hence, while the circumferential parts of the planets next to the sun revolve from west to east, the sun apparently revolves from east to west, as is manifest from the motion of the dark spots across the solar disk.

That the circumferences of moving circles rotate about

their centres in contrary directions at opposite extremities of their diameters is an axiomatic truth which finds its concrete expression in the diagram referred to. This geometrical relation is also practically illustrated in the reaction steam engine of Hero of Alexandria, in which a hollow globe is made to revolve by two jets of steam issuing in contrary directions from opposite extremities of its diameter. Other instances of direct and retrograde motion may also be seen in the catherine wheels of ordinary firework displays, and in hydraulic turbines with multiple jets around the circumferences.

Halley's original conception of concentric spheres rotating within the earth, with a differential motion, is fruitful in leading to the further idea that the ejection of comets from a planet may be periodic from causes within itself, in like manner to the eleven years maximum sun-spot ejections of elementary gaseous substances\*. For it is only necessary to assume that, after the ejection of cometary matter through the double thickness of two concentric shells, the differential motion would retard, or wholly prevent, the further discharge until the vents were again coincident.

The planet Jupiter, from his vast dimensions, is the most interesting member of the solar system for the study of planetary and cometary evolution. The great red spot on his surface is generally considered to be caused by luminous vapours at great depths within the globe, if not by the actual incandescent crust of that part of the planet. The great extent and permanency of this spot indicate it as the locus of one of the vents through which comets and cometary satellites have been ejected at different periods of the history of the planet.

It is now generally recognized that certain groups of periodic comets are associated in some way unknown with the larger planets respectively; the comets of short period belonging to Jupiter, as nearest the sun, and the long period comets (of which Halley's is the most notable member) to Neptune and intermediate planets.

All the motions of periodic comets are well explained on the assumption of their moving in elliptical orbits more or

\* Repeated attempts have been made to establish a causal connexion between the periodic times of Jupiter and sun-spot frequency. The absurdity of this notion is at once apparent from the fact that the sun rotates on his axis about 173 times during one revolution of the planet and, consequently, every part of the solar surface is presented in succession through nearly every two degrees of the Jovian orbit. The like demonstration is equally applicable to other members of the solar system.—H. W.

less elongated, but the vast tabulated periodic times of comets supposed to move in parabolic and hyperbolic curves are necessarily ultra-speculative.

As the attraction of solar gravitation extends far beyond the orbit of Neptune, the motion of a body on the line of an open curve would ultimately be arrested, and a comet would necessarily return over the same track, approximately, with a retrograde motion as an unknown member of the solar system. Halley's comet, however, is considered to move in an elliptical orbit, and has, therefore, the longest periodic time of which astronomers have certain knowledge.

As the principle of conservation holds good alike for celestial and terrestrial bodies, the moving force of comets will not exceed the attraction of gravitation beyond the limits of the solar system, and will be much less through the conversion of molar into molecular motion by friction of the discrete particles of cometary matter among themselves during the act of ejection, as also from the resistance of the medium through which they move in their orbits, and especially near the sun.

The principle of conservation, as will be obvious, will hold equally for the comets ejected from the planets of other stellar systems. Hence the absurdity of bringing cometary bodies into the solar system which contains within itself the power of evolving its own comets. Moreover, it will be further evident that this immigration motion might be extended to include the earth and other planets as bodies from other stellar systems, captured by the sun in their wanderings from outer space.

Jupiter, with his system of satellites, is generally regarded as a miniature solar system formed by the successive condensations of a nebular substance surrounding the planet. The laws of attraction, moving force, and Kepler's laws have the same relations among his satellites as in the planetary system. The binary progression of the periodic times of the three adjoining major satellites, Io, Europa, and Ganymede (which are very nearly in the ratio of 1, 2, 4), indicates an orderly process of evolution similar to that of the binary progression of the planetary distances.

The erratic movements and irregular orbits of the three outer Jovian satellites recently discovered have, however, presented a new problem for solution in connexion with the nebular theory of the evolution of satellites, as it was found that the orbital motion of the outermost one was in a retrograde direction.

An attempt has been made to explain the anomaly by

assuming that Jupiter at an earlier period of his history performed a semi-revolution about his polar axis, and that all the inner satellites turned over, in like manner, in opposition to the orbital direction of their erratic outer member.

An insuperable objection to this ingenious hypothesis is the absence of any causal connexion between the assumed inversions of the axial motions of planets, together with their satellites, and their orbital revolutions, and, consequently, leaves untouched the problem of the retrograde orbital motion of a satellite, which it is the precise object of the hypothesis to explain. The fallacy involved in the scheme will at once be apparent when applied to the orbital rotations of all the planets which are clearly independent of the positions of their axes of rotation in relation to the plane of the ecliptic. And here it may be useful to apply Newton's 'First rule of reasoning in philosophy,' as laid down in the 'Principia' that, "we are to admit no more causes of natural things than such as are both true and sufficient to explain their appearances; for Nature does nothing in vain, and more is in vain when less will serve, for Nature is pleased with simplicity, and affects not the pomp of superfluous causes."

I have already said that when a comet is ejected from a planet opposite to the orbital motion its direction would be retrograde to that of the planet from which it was ejected.

The orbital velocity of Jupiter being eight miles per second, a body ejected from its interior at a much greater velocity (which I will call the critical velocity) would, by the diminished attraction of the planet, conjointly with the action of solar gravity, revolve with a retrograde motion in an irregular and much enlarged orbit in accordance with the observations (Pl. XIV. fig. 1). And if ejected with a velocity much greater than that necessary to retain it within the sphere of the planet's attraction, the body would move in a separate and elliptical orbit as a comet.

Considering the comparative minuteness of Jupiter's three outer satellites, which are estimated to be less than thirty miles in diameter, and that the orbits of J. VI. and J. VII. are both inclined at  $30^\circ$  to the plane of the ecliptic, and have nearly the same periodic times and distances, these small bodies are hardly entitled to rank as satellites, but may rightly be regarded as planetary ejectamenta. Nevertheless, the discovery of them is of great importance, as furnishing another indirect proof of the planetary origin of comets.

Applying the foregoing principles of direct and retrograde motion of cometary bodies to the explosion of a whole planet between Mars and Jupiter, the fragments projected opposite to the orbital motion would be retarded, and by the action of solar gravity revolve in a smaller orbit than that of the planet before the explosion. On the other hand, the motion of the fragments coincident with the orbital direction would be increased, and by the diminished action of the sun's attraction, revolve in a larger orbit in accordance with the observations. In neither of these cases, however, would the orbits of the fragmentary bodies again intersect each other at the point of the planet's orbit where the explosion occurred.

All the observations which I have made on the evolution of the Jovian satellites and cometary ejecta, are applicable alike to the Saturnian and other systems of planetary satellites. The evidence of orderly progression in the periodic times of the inner satellites of Saturn differs in one respect from that indicated by the satellites of Jupiter in similar positions, as the times of revolution of the first and third satellites are in the ratio of 1 and 2, and the times of the second and fourth are also in the same ratio, as was first pointed out by Sir John Herschel\*.

Notwithstanding that the actual surface of Jupiter is covered with dense vapours of great depth, just as the terrestrial globe at one period of its history was enveloped with an atmosphere of aqueous vapour which has since condensed to form the oceans, several facts, in addition to those advanced, indicate that the Jovian planet has a solid crust of considerable thickness.

The remarkably bright round spots which suddenly appear on the planet at irregular intervals, and have been described by Lassell, and also by Dawes, as having some resemblance to lunar craters†, indicate considerable volcanic activity below the atmospheric envelope. The eruptive matter from the Jovian craters also produces the appearance of belts on his outer surface, as well as those seen on Saturn and Uranus. That these belts and bands are caused by volcanic dust ejected to great heights from the interior parts of planetary bodies is highly probable from observations made on the great eruption of Krakatoa in 1883‡.

The ejecta from this volcano reached a height of more

\* 'Outlines of Astronomy,' p. 368, 1864.

† Monthly Notices Roy. Ast. Soc. vol. x. 1850; *ibid.* vol. xviii. 1857.

‡ "The Eruption of Krakatoa and Subsequent Phenomena," Report of the Krakatoa Committee of the Royal Society, 1888.

than 30 miles, forming a belt  $20^\circ$  wide on each side of the equator, and made two successive revolutions round the globe in the course of twenty-five days. The optical phenomena attending the eruption also included blue, green, and copper-coloured suns, similar to the transient colours observed on the belts of Jupiter.

The problem of the origin of Saturn's rings has for a long time engaged the attention of natural philosophers, but no solution has yet been offered of sufficient importance to gain the general assent of astronomers. The first of these attempts was made in 1755 by Kant in his 'Natural History and Theory of the Heavens,' wherein he assumes that Saturn at an early period of its history had the characteristics of a comet, and moved in an orbit of great eccentricity. That its tails gradually contracted upon the planet to form a cometic atmosphere of vapours which subsequently changed into the form of a ring entirely separated from the body of the planet.

In the 'Système du Monde' of Laplace the rings are supposed to be the original nebular substance uncondensed into the form of satellites. This opinion has since been strongly held by astronomers and other scientific investigators, and utilized as an illustration of the nebular theory of the origin of planetary systems.

Recent spectroscopic and mathematical investigations have, however, shown that the rings consist of a vast number of minute bodies, in confirmation of the views previously advanced by J. D. and J. Cassini in the 'Memoirs of the French Academy of Sciences,' in 1705 and 1715.

In neither of the explanations of the origin of Saturn's rings by Kant and Laplace is there any suggestion of the interior of the planet as being the birthplace of these singular appendages. It is therefore with some amount of diffidence that I venture to affirm that they are the ejectamenta of Saturn when its diminishing energies were insufficient to eject a cometary satellite, or a comet with its train of meteorites beyond the sphere of its gravitational attraction. And here it may be well to remark that all meteoric and other small discrete bodies are not formed *directly* from the universal nebular substance, but are necessarily fragments of the solid or liquid parts of a globe, which had a long previous history, involving the evolution of the several series of elementary substances of which the globular body was composed.

The dimensions of Saturn's rings are drawn up in the following table for a new determination of the times of their

revolutions, and are based upon the commonly accepted equatorial diameter of the planet = 73,860 miles or the semi-diameter of 36,930 miles.

### ELEMENTS OF SATURN'S RINGS.

	Distance from centre of Saturn.		Time of Revolution.
Rings.	Sat. Units.	Miles.	h. m.
Exterior A .....	2.30	84,937	12 48
Breadth .....	0.26	9,602	" "
Mid-breadth .....	2.17	80,138	11 45
Interior A .....	2.04	75,337	10 42
Interval .....	0.07	2,585	" "
Exterior B .....	1.97	72,752	10 9
Breadth .....	0.47	17,357	" "
Mid-breadth .....	1.735	64,073	8 24
Interior B .....	1.50	55,395	6 44
Exterior C .....	1.50	55,395	6 44
Breadth .....	1.23	8,493	" "
Mid-breadth .....	1.385	51,148	6 00
Interior C .....	1.27	46,901	5 15
Ball Space .....	0.27	9,971	" "
Sat. Ball .....	1.00	36,930	10 13
Mimas.....	3.36	124,084	22 37

The dimensions have been calculated from scaled measurements which I have made of reproductions of the fine photographs of Saturn taken at the Lick\* and other observatories during recent years, and which surpass in accuracy those calculated from observations and micrometric measurements.

The radial dimensions of the rings on the line of the equatorial diameter of the planet have the same proportional relations at different angles about this diameter, and constitute the basis of the method of measurements which I have adopted.

In accordance with the notation of O. Struve, now generally adopted, I have designated the rings A, B, and C in the order of their distances from the planet (Pl. XIV. fig. 2).

\* Todd, 'Stars and Telescopes,' 1900.



The velocity with which a body is ejected from the interior of a planet, as I have said, determines whether it shall be designated a comet, a cometary satellite, or a cometary ring. If the latter, it will be obvious that, from whatever part of the circumference of the planet the discharge takes place, the ejected matter will necessarily move in the same direction as the axial rotation. Moreover, if the discharge continued without interruption during one or more rotations of the planet a complete ring of discrete bodies would be formed in accordance with the accepted theory and observations.

It will be further evident from the three orders of cometary discharge specified above, that the formation of the outer ring A preceded that of the next inner ring B, as shown by the interval of 2585 miles of clear space between them.

That the second ring was formed some time subsequently to the first, is highly probable from the long period of intermittent discharges observable in terrestrial volcanoes, and also in celestial explosive action, of which there are abundant instances in planetary volcanoes and variable stars.

That the third and dusky ring C of Saturn represents its last and final effort of cometary evolution is shown by the wide separation of the discrete bodies of which the ring C is composed, and further indicated by its semitransparency through which the body of the planet is distinctly visible.

I have not included in the table of distances the now well-recognized subdivisions of the exterior ring A and of the dusky ring C, so distinctly seen in the photographs, but they are sufficiently definite for a measurement to be taken of their width, which is approximately 230 miles.

The thickness of the rings is difficult to determine on account of the great distance of Saturn from the earth, and has been estimated by Herschel as not exceeding 250 miles. Assuming this value to be approximately correct, the vent in the crust of the planet through which the matter of the rings was ejected may not have been larger than those from which it is assumed the outer satellites of Saturn and Jupiter were also ejected.

The polar compression of Saturn is well determined by the photographic method when the edge of the ring alone is visible, and is in the ratio of 10 to 11 of the equatorial diameter. The value of the compression from good observations varies between  $\frac{1}{9.02}$  and  $\frac{1}{10.19}$ .

Turning now to the times of revolution of Saturn's rings respecting which there are wide differences of opinion, arising

from the fact that there are no distinctive marks on their surfaces from which their rotations can be determined.

Laplace and also Herschel were content to consider the rings as one body, and both assigned the period of its rotation to be 10 hours 32 minutes, as being the time of a satellite revolving at the same distance as the middle of its breadth.

Later investigators have, however, found it necessary to recognize, from the discrete constitution of the rings, the different times of revolution of their outer and inner circumferences, but have still treated them as one body, and assigned a period of 12 hours 5 minutes for the outer circumference, and 5 hours 50 minutes for the inner edge of the dusky ring C.

From the fact that the ring A is separated from the inner ring B by a clear space of 2585 miles, the time of its revolution may be determined independently of the times of B and C.

As the ring A is postulated to be the first annular ejection from the planet, its outer edge would be the extreme limit of the ejective force, and it would consequently revolve in the same time as a satellite at the same distance, in accordance with Kepler's third law. Now the period of Mimas, the first satellite of Saturn, is 22 hours 37 minutes, hence we have for the outer edge of the ring a periodic time of 12 hours 48 minutes; and 11 hours 45 minutes as the time of rotation at the middle of its breadth.

Dealing with the second ring B in the same manner, we have for the outer edge a period of 10 hours 9 minutes, and for the middle breadth, 8 hours 24 minutes as the period of revolution.

The determination of the time of revolution of the dusky crape ring C presents some difficulty on account of the wide separation of the discrete particles of which it is composed, and its apparently close contact with the interior of the ring B, but as by Kepler's law the time of revolution of the interior of B would be 6 hours 44 minutes, the exterior parts of C may be assumed to revolve at the same rate, and the inner edge of C in 5 hours 15 minutes.

From the principle of the transformation of energy it may be rightly inferred that some of the molar motion of the vast assemblage of discrete particles constituting the rings would be converted into heat, with a consequent slow contraction of their orbits. The observations collected by O. Struve in favour of such contraction have been discussed by astronomers, but without so far arriving at any definite conclusion.

The resemblance of Saturn's rings to the Zodiacal Light is briefly indicated by Kant in a short chapter of his 'Theory of the Heavens,' in which he accounts for its origin by assuming that the fire of the sun raises from its surface vapours similar to those which formed Saturn's ring, and by their motion around the sun formed an expanded plain in the plane of the sun's equator, or in the figure of a convex lens.

Modern investigators have since carefully observed this singularly interesting object, and mostly agree that it is a vast accretion of cometary and meteoric particles from outer space and extending beyond the earth's orbit, but none of them, so far as I know, has suggested the interior of the sun as the place from which the Zodiacal substance has been ejected.

That cometary and meteoric matter may have contributed to the volume of discrete bodies surrounding the sun and extending to some distance within the orbit of Mercury has some degree of probability in its favour, but the extreme tenuity of the outermost parts of the Zodiacal substance, together with its immense distance from the central body, appears to me to be better accounted for on the supposition of its consisting of the lighter elementary substances in a state of extreme sub-division ejected during solar eruptions, as in the instance of the ejection of enormous masses of hydrogen observed by Young which I have already adduced.

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LXXIV. *Limitations imposed by Slip and Inertia Terms upon Stokes's Law for the Motion of Spheres through Liquids.*  
*By H. D. ARNOLD, Fellow in Physics in the University of Chicago\*.*

RECENT investigations have shown that Stokes's law for the motion of spheres in fluids is less general in its applicability than has hitherto been assumed. The importance of these investigations has lent interest to a determination of the limits within which the law may be applied, and of the error introduced when these limits are exceeded. Liquids of moderate viscosity lend themselves most readily to determinations of this kind, since in them spheres of considerable size will move with easily measurable velocities, and especially since the viscosities of these liquids may be very simply found with a high degree of accuracy. It is the

\* Communicated by Prof. R. A. Millikan.

object of this paper to discuss the departures from Stokes's law due to the velocity of the spheres and to slip at the interface of sphere and liquid.

The force which opposes the steady motion of a sphere through a viscous liquid as deduced by Stokes\* on purely theoretical grounds is given by

$$F = 6\pi\mu rv,$$

where  $\mu$  is the coefficient of viscosity of the fluid,  $r$  the radius of the sphere, and  $v$  its velocity. From this it follows that if a sphere of density  $\sigma$  is moving in a liquid of density  $\rho$  and is acted on by no external force except gravity, since its motion will become steady when the impressed force is balanced by the viscous resistance, that is when

$$\frac{4}{3}\pi r^3(\sigma - \rho)g = 6\pi\mu rv,$$

its terminal velocity will be given by

$$v = \frac{2}{9}gr^2\frac{\sigma - \rho}{\mu}.$$

In the mathematical derivation of the original formula certain assumptions are made, notably

1. That the discontinuities of the fluid are small compared with the size of the sphere.
2. That the fluid is infinite in extent.
3. That the sphere is smooth and rigid.
4. That there is no slip at the surface between sphere and fluid.
5. That the velocity of the sphere is small.

Cunningham † has investigated theoretically, and Millikan ‡ experimentally, the effect of a violation of the first assumption, and they have shown that in the case of a very small sphere falling in a gas, there is a considerable departure from the value given by the original formula. In the present investigation, however, we are dealing only with liquids, and with spheres of comparatively large size, so that we may consider this assumption as sufficiently justified.

The second assumption has been investigated both theoretically and experimentally by Ladenberg §, who found that

\* G. G. Stokes, *Mathematical and Physical Papers*, iii. p. 59.

† Cunningham, *Proc. Roy. Soc. ser. A*, lxxxiii. pp. 357-365 (March 1910).

‡ *Phys. Rev.* April 1911.

§ R. Ladenberg, *Ann. der Phys.* xxii. p. 287 (1907), and xxiii. p. 447 (1907).

if the liquid is contained in a cylinder of circular cross-section of radius  $R$ , and of length  $L$ , the simple formula should be modified to read

$$V = \frac{2gr^2(\sigma - \rho)}{9\mu\left(1 + 2.4\frac{r}{R}\right)\left(1 + 3.1\frac{r}{L}\right)}.$$

Using this corrected form he examined the viscosity of Venice turpentine, using a series of steel spheres, and obtained the value 1343, whereas the value found by the capillary tube method at the same temperature was 1325. This seems to have been the first direct comparison of these two methods, and their agreement to within 1.3 per cent. shows the validity of the corrected formula in the case of liquids of very high viscosity. As Ladenberg points out, this boundary effect may account for the results obtained by O. Jones\*, who used spheres of mercury in glycerine, and found viscosity values so high as to cast considerable doubt on the validity of Stokes's law.

Experiments with liquids of low viscosities were carried out by Allen†, using air bubbles, and spheres of amber and paraffine, in water and in aniline. His results vary widely among themselves, but in general seem to confirm the simple formula. With the air bubbles in aniline, however, the velocities observed were uniformly higher than those computed. This is more striking when we consider that the formula should give the MAXIMUM terminal velocity (provided there is no surface slip). If, instead of the value of  $\mu$  used by Allen, we substitute the more probable one obtained by extrapolating from Wijkander's‡ tables to the temperature  $9^{\circ}8$  at which Allen worked, we find his values for the observed velocities to be from 10 per cent. to 30 per cent. higher than those calculated, a departure not easily attributable to experimental errors.

Allen also investigated the effect of increase of size upon the terminal velocities, but as most of his observations were

\* O. Jones, *Phil. Mag.* xxxvii. p. 451 (1894). Cf. also K. Schottner, *Beibl.* iii. p. 60.

Note: I have repeated these experiments using solid spheres, and have obtained the following values for the viscosity of glycerine:—

Temperature . . . .	$-9^{\circ}8$	$-5^{\circ}2$	$2^{\circ}7$	$6^{\circ}0$	$20^{\circ}0$	$22^{\circ}0$	$30^{\circ}0$
Viscosity . . . . .	188	105	42.2	27.6	13.7	7.61	3.43

That these values are on the whole a little lower than Schottner's may be due to impurities in the glycerine, as no precautions were taken to guard against traces of water.

† *Phil. Mag.* l. p. 323 (1900).

‡ *Beibl.* vii. p. 11 (1879).

with radii so great that Stokes's law no longer held even approximately, they do not serve to define the region of validity of the simple formula.

As to the existence of surface slip, experimenters seem about evenly divided. In general, however, the more sensitive the experimental method used, the smaller the assigned value of the coefficient has become. If, instead of the coefficient of slip, we use the coefficient of sliding friction, the form of Stokes's law becomes\*

$$V = \frac{2gr^2(\sigma - \rho)}{9\mu} \left[ 1 + \frac{\mu}{\beta r + 2\mu} \right],$$

which for  $\beta$  infinite reduces to the original form, but for  $\beta$  zero gives a value 50 per cent. higher. We see at once that if  $\beta$  has a finite value, even though it be very large, this correction factor should become appreciable for a sphere of sufficiently small radius in a liquid of high viscosity. This gives a very sensitive method of detecting the presence of slip, somewhat similar to that used by Whetham† in the analogous case of flow through tubes. It has hitherto suffered under the disadvantage that no experimental verification of this theoretical correction factor has seemed possible. The proof of the correctness of the factor in the case of air bubbles, however, where, as will be shown later, the apparent value of  $\beta$  may be nearly zero, completely removes this objection, and allows the use of the formula to determine  $\beta$ .

Condition (5) is imposed to simplify the mathematical analysis, since it allows us to neglect terms of the order of the square of the velocity. These terms have been called the inertia terms. It can be shown that the solution may be expected to hold only when the velocity is small compared with  $\frac{\mu}{\rho r}$ ‡. The value of  $r$  for which  $v = \frac{\mu}{\rho r}$  is called the critical radius, and will be designated by  $\bar{r}$ . Various observers have assumed that the upper limit of radius for which the simple formula may be used is of the order  $\frac{\bar{r}}{10}$  (Ladenberg), to  $\frac{\bar{r}}{\sqrt{10}}$  (Zeleny).

It is the first object of this experiment to find the upper radius limit of applicability of the simple law in terms of  $\bar{r}$ .

\* Basset, *Treatise on Hydrodynamics*, vol. ii.

† *Proc. Roy. Soc.* xlviii. p. 225 (1890).

‡ Lamb, *Hydrodynamics*.

*Method and Apparatus.*

If from the observed times of fall of spheres of various sizes we compute the apparent viscosity coefficient of the liquid by Stokes's law, and if we plot these values as functions of the radii, we should be able to determine the radius at which the computed values begin to depart from the actual value as determined directly by the capillary tube method.

*Spheres.*—Among the kinds of spheres used may be mentioned mercury, platinum, iron, Rose metal, wax, spheres of oil in water, and spheres of water in oils. Mercury proved unsatisfactory for several reasons, especially because of the difficulty in diameter measurements. Iron and platinum spheres could be obtained only in large sizes, and were used merely to check other observations. The most satisfactory results were obtained with spheres of wax and of Rose metal. The method of making these spheres will be referred to later.

*Temperature.*—As the change of viscosity with temperature is very rapid in the more viscous oils, it is important that the temperature be maintained constant to within at least one-tenth of a degree during the experiments. This was done by means of an electric heater and a fan for maintaining the circulation of the air. With this arrangement the temperature as shown by a thermometer strapped to the fall tube could be maintained with the desired degree of accuracy for indefinite periods, providing that the room was always slightly warmer than the outdoor air.

*The Fall Tubes.*—Three glass tubes were used of lengths about 70 cm., and of internal radii  $A=0.22$  cm.,  $B=0.547$  cm.,  $C=1.63$  cm. These were etched with fine lines as nearly as possible at right angles to their axes, and were mounted vertically in adjustable supports. With the adjustment properly made the spheres fell very accurately along the axes of the tubes, but check experiments showed that even a very considerable deviation from an axial course produced no noticeable change in velocity.

*Velocity.*—To comply with condition (5) it is necessary to work with small velocities. There are three factors by which this may be brought about; a liquid may be chosen with a very high coefficient of viscosity; the spheres used may be of nearly the same density as the liquid; or spheres may be used of extremely small radii. In practice these three factors must be so balanced as to minimize the total error introduced in the three measurements. In timing a stop-

watch was used, and thus considerable chance of error was introduced in the case of short fall times. In general the times may be considered accurate to the nearest fifth of a second, although the occasional errors must be much greater than this.

*Density.*—The densities of the oils were found by the pyknometer method at the temperature at which they were used. The methods of determining the densities of the spheres will be referred to later. It is important to notice that it is the difference of the densities of the sphere and of the liquid that occurs in the formula. If, therefore, we attempt to obtain small velocities by making  $(\sigma - \rho)$  small, we must make the density determinations with great precision, and the question of the homogeneity of the spheres becomes of importance.

*Radius.*—Radii measurements were made with a micrometer microscope just before each sphere was placed in the fall tube. With spheres of the size used there is little chance of error unless the surface is highly reflecting, as is the case with mercury.

*Viscosity.*—A very simple form of Poiseuille's apparatus proved sufficiently accurate for this purpose. A glass tube 2.2 cm. in internal diameter and 45 cm. long was bent at right angles near one end, and fitted with a perforated stopper through which a capillary tube could be inserted. With the capillary clamped in a horizontal position, the vertical tube was filled to a height " $h$ " with the liquid under investigation. By placing a beaker in contact with the tube near its outlet the liquid flowed steadily down the side, obviating any error which might be introduced by the formation of drops. Experiments with different heads of the liquid showed the back pressure to be negligible. To guard against errors due to irregularities in the capillary bores two tubes were chosen, their average internal diameters were found by mercury columns, and they were then checked against each other by a determination of the viscosity of colza oil. The Table I. (p. 761) shows that the values agree as closely as could be expected from the probable errors in height and temperature measurements, and justifies the use of either tube separately.

#### *Rose Metal in Colza Oil.*

The Rose metal spheres were made from metal cast a number of years ago for another purpose. It had been turned up in two cylinders, and hence its density could be



TABLE I.

Capillary.	Radius.	Length.	" <i>h</i> ."	Time.	Mass.	$\mu$ .
I. ....	·09275	74·35	36·9	600	10·241	·6958
I. ....	"	"	"	"	10·263	·6943
I. ....	"	"	"	"	10·289	·6953
I. ....	"	"	23·0	"	6·387	·6954
II. ....	·05624	62·50	39·5	1000	2·946	·6939
II. ....	"	"	"	"	2·933	·6971
II. ....	"	"	"	"	2·943	·6946
II. ....	"	"	"	"	2·929	·6980
II. ....	"	"	"	"	2·937	·6962

Average  $\mu = 0\cdot6956 \pm 0\cdot0024$ .

determined from its computed volume as well as by weighing in air and in water. The average density thus determined was  $9\cdot718 \pm 0\cdot003$ .

This metal melts at about  $82^{\circ}$  C. and is quite fluid at the temperature of boiling water. It was placed in a small test tube drawn out to form a short capillary, and the whole suspended in a glass tube about 70 cm. long and 3 cm. in diameter. The large tube was then filled with water, and heat was applied in such a way that the upper end was kept at  $100^{\circ}$  C. while the lower end was at about  $60^{\circ}$  C. The molten metal was forced out by compressed air, and settled in the form of spray, the drops being sufficiently cooled to maintain their spherical shape by the time they reached the bottom. The success of this method depends on the relatively slow motion of the spheres, and on the slight temperature gradient of the water through which they fall. The slow and uniform cooling tends to produce homogeneity of structure, while the low velocities allow the retention of an almost perfectly spherical shape. With a capillary of the proper size a single casting gave a large number of spheres with radii from  $\cdot002$  cm. to  $\cdot1$  cm. Many of these spheres showed surface pits, but from the large number prepared it was not difficult to pick out sufficiently perfect specimens of any desired size. Check experiments with badly pitted surfaces showed, however, that no appreciable change in velocity could be attributed to these surface irregularities.

In a series of observations with these spheres the temperature was maintained as nearly as possible at  $21^{\circ}\cdot4$  C. At this temperature the density of the colza oil is  $\cdot9166$ . In

the table of results (Table II.) column 3 gives the values of  $\mu_s$  computed from the simple formula, and column 4 the value  $\mu_L$  given by Ladenberg's corrected form of the equation. Tube B was used, the length of fall being 53.4 cm.

TABLE II.

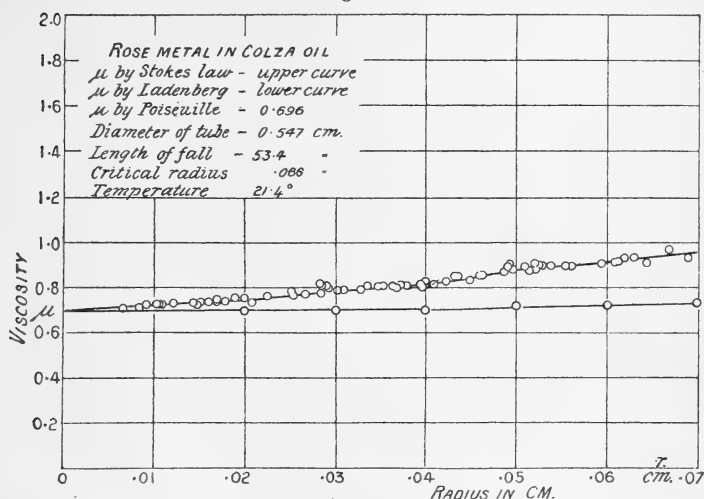
Rose Metal spheres in Colza oil. Length of Fall 53.4 cm.

Radius of Sphere in cm.	Time of fall in sec.	Visc. by Stokes's law.	Corrected value by Ladenberg's formula.	Radius of Sphere in cm.	Time of fall in sec.	Visc. by Stokes's law.	Corrected value by Ladenberg's formula.
0.0704	5.3	0.941	0.714	0.0372	16.4	0.813	0.699
0.0690	5.5	0.938	0.721	0.0368	16.5	0.801	0.689
0.0668	6.1	0.975	0.755	0.0363	17.0	0.803	0.693
0.0644	6.2	0.922	0.719	0.0355	17.4	0.804	0.696
0.0630	6.6	0.939	0.736	0.0351	18.1	0.801	0.694
0.0619	6.8	0.934	0.735	0.0348	18.6	0.807	0.700
0.0613	6.8	0.916	0.722	0.0335	20.0	0.804	0.701
0.0609	6.9	0.917	0.724	0.0329	20.4	0.791	0.691
0.0594	7.1	0.898	0.712	0.0310	22.9	0.789	0.694
0.0562	7.9	0.894	0.718	0.0301	24.2	0.786	0.694
0.0554	8.2	0.902	0.726	0.0292	26.1	0.798	0.707
0.0538	8.6	0.892	0.722	0.0289	25.9	0.775	0.688
0.0530	8.9	0.896	0.727	0.0285	26.5	0.771	0.686
0.0525	9.1	0.899	0.731	0.0284	26.8	0.775	0.689
0.0523	9.0	0.882	0.718	0.0283	27.4	0.787	0.699
0.0522	9.3	0.910	0.741	0.0267	32.7	0.835	0.748
0.0515	9.2	0.875	0.713	0.0254	32.9	0.761	0.685
0.0510	9.6	0.895	0.731	0.0252	34.5	0.785	0.707
0.0497	9.9	0.876	0.720	0.0227	41.3	0.763	0.694
0.0494	10.4	0.910	0.747	0.0224	42.4	0.763	0.695
0.0488	10.5	0.896	0.738	0.0209	47.1	0.737	0.675
0.0487	10.2	0.867	0.764	0.0208	47.0	0.729	0.668
0.0468	10.7	0.840	0.697	0.0200	52.2	0.748	0.688
0.0467	11.2	0.875	0.727	0.0190	58.7	0.759	0.701
0.0464	11.1	0.857	0.711	0.0178	64.3	0.730	0.678
0.0462	11.4	0.857	0.713	0.0171	68.8	0.721	0.671
0.0450	11.4	0.827	0.691	0.0168	73.6	0.745	0.693
0.0437	12.5	0.856	0.718	0.0164	76.5	0.737	0.688
0.0432	12.7	0.849	0.714	0.0161	79.8	0.741	0.692
0.0423	12.8	0.821	0.692	0.0151	90.9	0.743	0.697
0.0420	12.8	0.809	0.684	0.0147	93.6	0.725	0.681
0.0411	13.2	0.799	0.677	0.0144	99.3	0.738	0.694
0.0408	13.6	0.811	0.688	0.0143	99.8	0.733	0.688
0.0403	14.0	0.817	0.694	0.0110	167.0	0.724	0.691
0.0400	14.2	0.814	0.693	0.0104	188.1	0.729	0.698
0.0399	14.5	0.827	0.704	0.0102	195.5	0.729	0.698
0.0397	14.3	0.808	0.688	0.00912	242.8	0.724	0.696
0.0395	14.6	0.817	0.696	0.00651	469.0	0.712	0.692
0.0380	15.7	0.813	0.696				
0.0379	15.5	0.798	0.684				

Average of the last 50 observations in the last column 0.6930.

These results are shown graphically in fig. 1, the upper curve showing  $\mu_s$  and the lower  $\mu_L$ . It is seen that  $\mu_L$  remains approximately constant up to the radius  $r_1 = .042$  cm.

Fig. 1.



The average of the values for radii less than  $r_1$  gives 0.6930, agreeing closely with the value 0.6957 given by the capillary tube method. This is an excellent confirmation of the validity of Ladenberg's correction for an oil of less than 1/2000 the viscosity of Venice turpentine.

As it was conceivable that the rise of the lower curve might be due to the failure of Ladenberg's correction rather than to the influence of the inertia terms directly, a further test of the validity of the correction was made with tubes A and C. The results are plotted in figs. 2 & 3 (p. 764), where the curves have the same significance as in the previous figure, A and A', C and C', referring respectively to the values of  $\mu_s$  and of  $\mu_L$  obtained with the two tubes. The curve A' begins to rise at about  $r = 0.32$  cm., that is, when the ratio  $r/R$  is about 1/10. Since the tube is very small this rise is probably due to the failure of the correcting factor, hence it is not effective for values of  $r$  which make the ratio greater than this. With tube C the ratio becomes 1/10 only when  $r = 0.16$ , hence the rise of C' at  $r = .045$  can be attributed only to the inertia terms. This, it will be noted, is very nearly the value of  $r_1$  obtained with tube B. It would appear from this, since the computed value of  $\bar{r}$  is .066 cm., that the

inertia terms become effective when the radius is about seven-tenths of the critical radius.

Fig. 2.

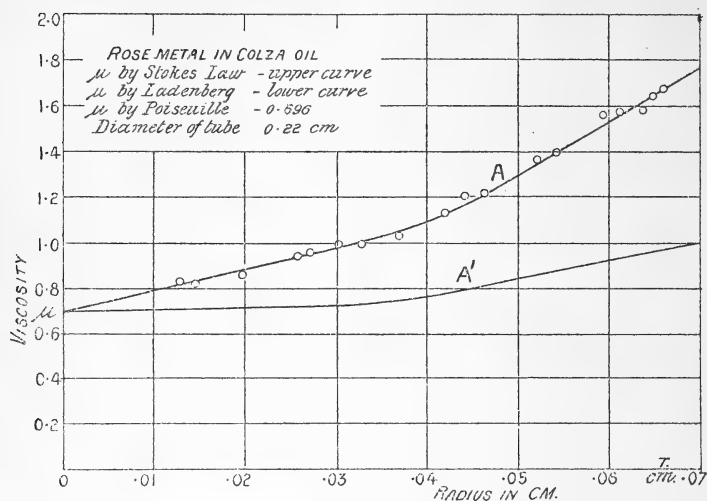
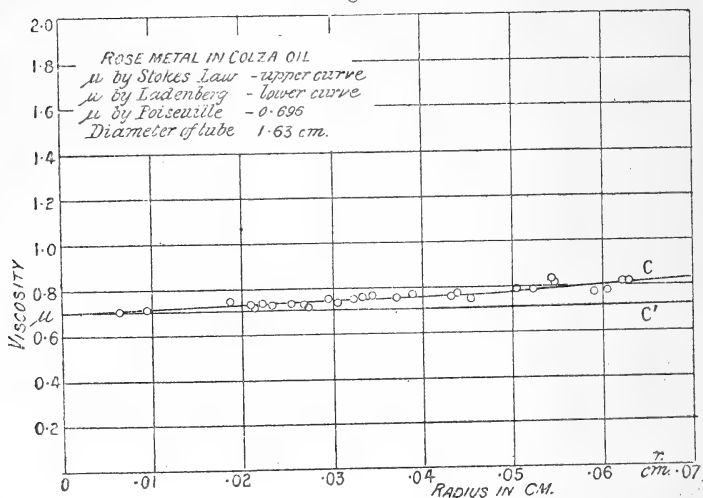


Fig. 3.

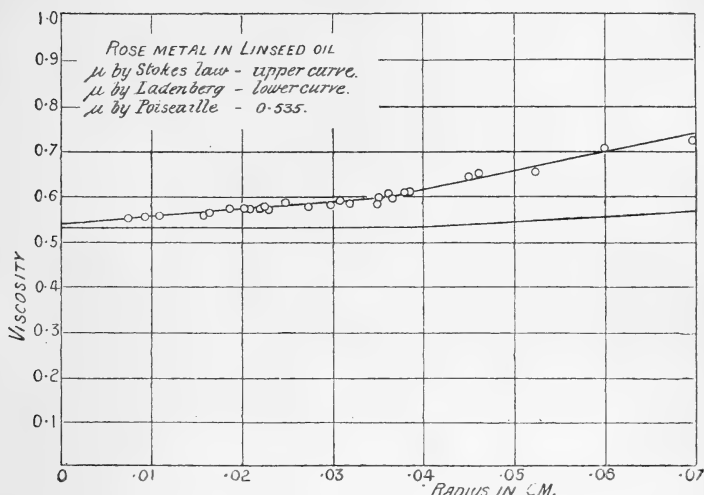


### Experiments with other Oils.

Experiments with linseed oil whose viscosity as found by Poiseuille's method was 0.535 gave results in close agreement

with those obtained with the colza oil. In fig. 4 it is seen that the lower curve begins to rise at about  $r=0.04$ . The rate of departure from the straight line is very nearly the same as in fig. 1.

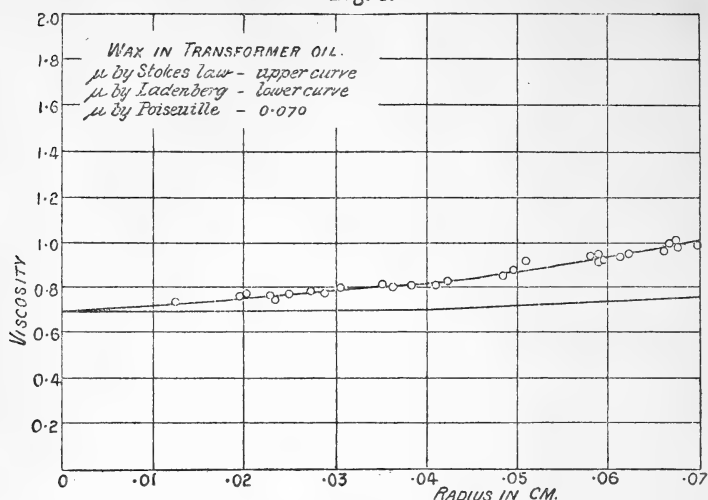
Fig. 4.



In working with oils of low viscosity it was necessary to have spheres of less density than the Rose metal. For this purpose some beeswax was melted in an alcohol-water mixture whose density was slightly less than that of the cold wax. The drops obtained by shaking the mixture cooled in very perfect spherical shape and proved to be of fairly uniform density. Their density was taken as that of an alcohol mixture in which they remained suspended, and was found to be  $0.9410$  at  $20^{\circ}0$  C.

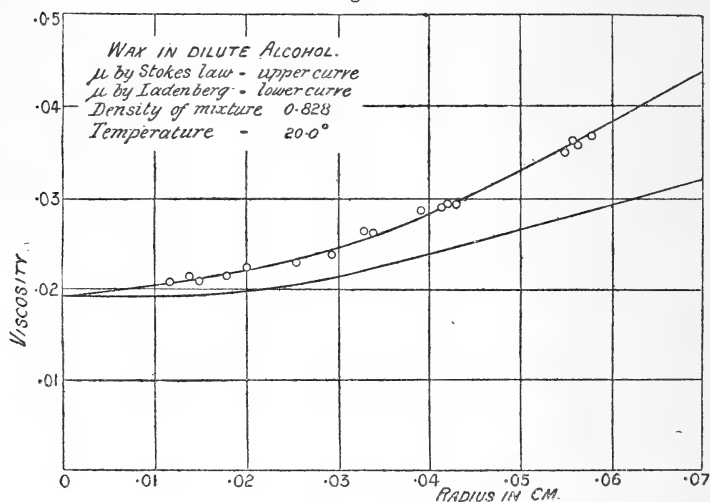
Results obtained with these spheres in a transformer oil of density  $0.837$ , and of viscosity  $0.070$ , are shown in fig. 5 (p. 766). The effect of the inertia terms becomes apparent at  $r=0.042$  as in the previous cases. The discrepancies among the observations in this case are easily accounted for by the possible variations in the density of the different spheres, since  $(\sigma-\rho)$  is only  $0.113$ , and a variation of  $0.1$  per cent. in density would make a difference of one per cent. in the result.

Fig. 5.



In fig. 6 are shown the results of similar experiments in a mixture of alcohol and water of density 0.828 at the temperature 20° C. Here the deviation from the straight line

Fig. 6.



comes at  $r=0.016$  cm. The terminal value of the curve at  $r=0$  gives as the viscosity of the mixture .0190, which is in agreement with the value given by Traube for a mixture of this density.

Table III. summarizes these results, giving the viscosities, the computed values of  $\bar{r}$ , the radii  $r_1$  at which the inertia terms become apparent, and the ratio of these last two, which gives the upper limit of applicability of the formula in terms of the critical radius. Through the range of viscosities covered, this upper limit seems to be independent of the coefficient of viscosity.

TABLE III.

	Viscosity.	Critical Radius $\bar{r}$ .	$r_1$ .	$r_1/\bar{r}$ .
Colza oil .....	·695	·066	·042	·61
Linseed oil .....	·535	·054	·040	·74
Transformer oil .....	·070	·068	·043	·63
Alcohol and water ...	·019	·026	·016	·62

*Surface Slip.*

In no case was there any tendency for the value of  $\mu$  computed from the motion of the spheres to fall below that obtained by Poiseuille's method. This means that even for the smallest spheres used the factor

$$1 + \frac{\mu}{\beta r + 2\mu}$$

does not differ from unity by more than the errors of observation. In the case of colza oil, where the smallest radius used was ·0065 cm., if we assume that a deviation of 2 per cent. due to slip could have been detected we see that  $\beta$  must be greater than 5000.

Of the several observers who have obtained values for  $\beta$ , Petroff\* has assigned to it the largest, namely 700. With this value the smallest sphere used in colza oil should have given  $\mu$  about 10 per cent. less than the actual value, a deviation which could not have escaped detection. The evidence that the value of  $\beta$  is higher than that obtained by Petroff is not as conclusive as could be desired, for it is conceivable that the roughness of the surface of the spheres may have influenced the results. But as the surfaces appeared fairly smooth under the microscope, and especially as after the most careful polishing there must

\* *Fortschr. der Phys.* vol. i. 1897, p. 391.

always remain irregularities of molecular size which might still be efficient in preventing slip, it does not seem unreasonable to compare these results with those obtained with somewhat more highly polished surfaces. A further confirmation of the high value of  $\beta$  was found in experiments with the same spheres in castor oil of viscosity 7.0. The lack of evidence of slip in this case implies  $\beta$  greater than 50000. It should be remarked that as far as these or any previous experiments are concerned,  $\beta$  may still have a finite value, and indeed according to the kinetic theory of fluids it is inconceivable that it should be infinite. The experiments simply fix a limit which the value must always exceed, and it is quite probable that for sufficiently minute spheres this factor would become of importance. It is interesting to note the resemblance between the factor here used to correct for surface slip and that arrived at by Cunningham\* from a quite different standpoint.

In an attempt to investigate the slip at other surfaces, spheres of various liquids were used in liquids of nearly the same densities. But here another disturbing factor enters, as one quickly realizes when he watches the rise of a drop of alcohol through olive oil. The outer layer of the drop is dragged away by the oil, and eventually breaks up into a chain of minute droplets. This wearing away of the surface would give the same effect as surface slip, but seems to be more than offset by the accompanying distortion of shape. The net result is a great irregularity in the results with different spheres, and a computed value of  $\mu$  usually somewhat too high.

Some preliminary experiments on the simultaneous motion of air bubbles and mercury spheres in the same tube were made in the hope that by thus entirely obviating the temperature factor, the method might be made sufficiently sensitive to detect much smaller slip effects. It at once appeared that the apparent slip at the surface of the air bubble was infinite in some liquids and zero in others. This wholly unexpected phenomenon gives us a method of verifying the correctness of the theoretical slip correction factor.

For this purpose a tube 2.4 cm. in internal diameter, and 27 cm. in length, was sealed to a narrow tube about 10 cm. in length and the outlet fitted with a glass stopper having a fine capillary opening. This opening was sufficiently small to retain the liquid and assured atmospheric pressure throughout the tube. The narrow stem was for the purpose of retarding the motion of the bubble so that it might not be

\* *Loc. cit.*



admitted to the main tube until any turbulence introduced by inverting the tube should have subsided. The procedure then consisted in obtaining a small bubble in the stem, inverting the tube, and timing the transits across fine lines etched on the main tube. The tube was again inverted and the bubble allowed to come to rest when about one-third of the return distance had been traversed, where it was measured as it rested against the side of the tube. This completed one observation. The bubble was then returned into the stem and the operation repeated until, owing to its erosion, the bubble had become too small to follow.

The chief errors in this method are introduced in the measurement of the size of the bubble, and in the assumption of no circulation in the liquid. The flattening of the bubble against the side of the tube becomes noticeable with the larger bubbles, hence we have to restrict ourselves to small ones. The errors due to circulation need be feared only in liquids of low viscosity, for observations on small specks of lint introduced into the tube showed that the turbulence caused by slowly inverting the tube had, in the case of the more viscous liquids, completely vanished before the bubble had emerged from the stem. With the less viscous liquids, however, this is the main source of error.

The square of the radius of the bubble was found to diminish uniformly as the total distance traversed increased, the rate of decrease being independent of the velocity, that is, of the time. That this diminution is due to a surface erosion similar to that observed in the passage of the drop of alcohol through olive oil seems obvious, since a bubble would sometimes remain for several hours at rest and show no decrease in size, while one trip along the tube would result in a very marked decrease. The rate of decrease is quite different in different oils, but does not seem to depend primarily on the amount of air contained in the oil.

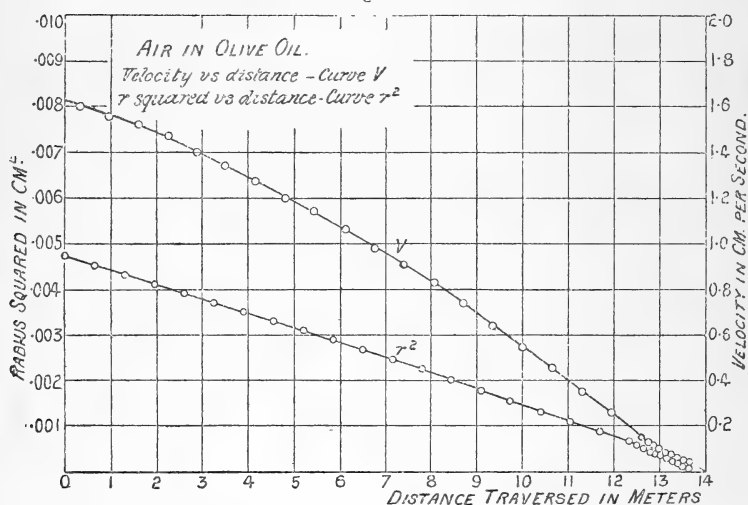
By plotting the squares of the radii as ordinates and the number of trips, or the total distance traversed, as abscissæ, we obtain a curve from which may be determined the probable radius at the time when the velocity was recorded. For most cases it is sufficient to take the radius as that given by the curve for the point half-way between the lines of transit. But with very small bubbles where the fractional decrease in radius is large for a single trip, a closer approximation is obtained by assuming the relation  $dr^2/dx = \text{constant}$ , and thus computing the probable radius. If  $a$  and  $b$  are the radii obtained from the curve for the first and second transits respectively, in any one observation, and if the ratio  $b^2/a^2$  is

called  $B$ , it follows on the assumption of Stokes's law that the radius of the constant sphere which would have traversed the distance in equal time is given by

$$A^2 = a^2 \cdot \frac{1-B}{\log_e 1/B}.$$

In fig. 7 the curve  $r^2$  shows the squares of the radii, and

Fig. 7.



curve  $V$  the velocities of a bubble of air in olive oil. The consistency of the observations allows a very accurate computation of the apparent viscosity. In fig. 8, curve I. shows the values of  $\mu$  computed from the simple form of Stokes's law, and curve II. shows the corresponding values after applying Ladenberg's correction. The upper and lower straight lines give respectively the values of  $\mu$  and of  $2/3 \mu$  from capillary tube measurements, the upper corresponding to no slip and the lower to infinite slip. It will be noticed that the observed values lie wholly within these latter two lines.

Fig. 9 shows similarly the results of an experiment with linseed oil. The observed values fall but slightly below those obtained with the capillary tubes, in marked contrast to the results with olive oil.

The curves of figs. 8 and 9 are typical of those obtained with all the liquids used. It would appear that in liquids of the type of olive oil the coefficient of slip is a function of the

radius, increasing with decreasing radius. A possible explanation of this might be looked for in the formation of a

Fig. 8.

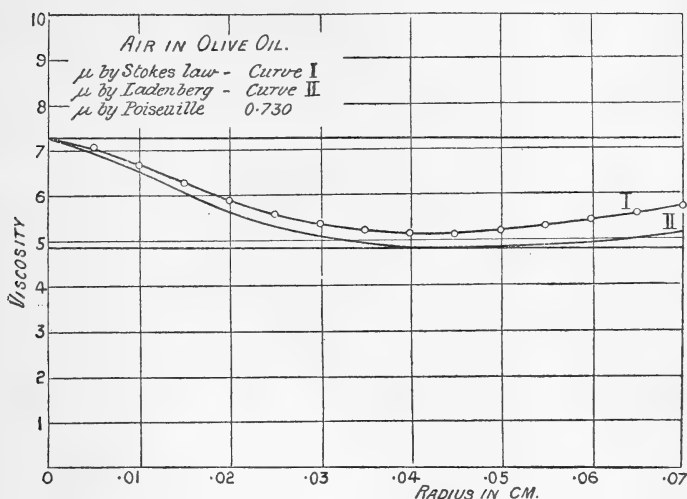
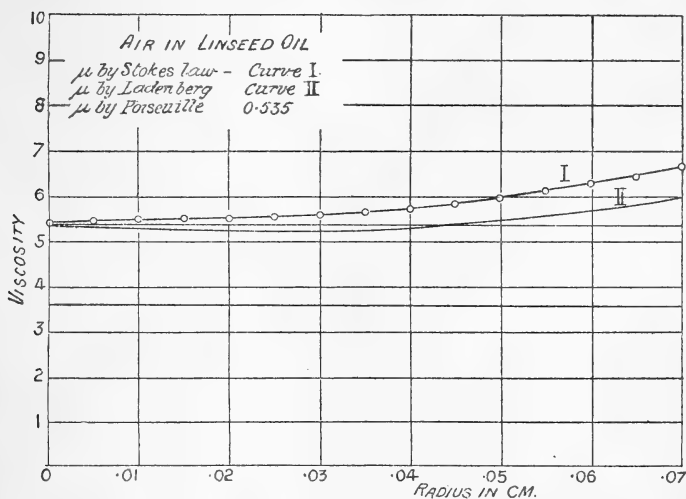


Fig. 9.



considerable thickness of film around the bubble which, as the bubble became smaller, might effectively increase its mass, and which would nevertheless remain unnoticed in the

diameter measurements. A simple computation shows, however, that the factor of increase in apparent viscosity due to a film of thickness  $t$  surrounding a sphere of radius  $r$  is  $t/r$ ; hence to account for the observed increase the thickness of the film would have to be equal to half the radius of the sphere. Moreover, on such an assumption the apparent viscosity would become abnormally large for very small radii, and this is not the case.

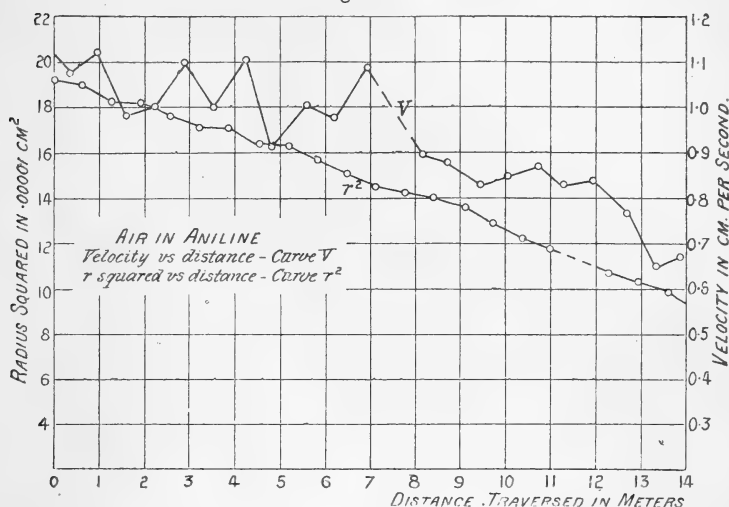
A more probable assumption seems to be that with large bubbles there is no appreciable film separating the air from the oil, but the oil next in contact with the air holds fast to a thickness of air approximately equal to the radius of the sphere of action of the oil molecules. The actually moving part of the air bubbles is therefore, on this assumption, moving in contact with a stationary air surface, and we would expect the coefficient of sliding friction to be the same as the coefficient of viscosity of the air. This latter value would be too small to detect in this experiment. If we assume, however, that as the sphere becomes smaller a film gradually forms, eventually enclosing the air in a permanent sack, we see that this sack would move upwards as a solid sphere, and we would have approximately the conditions of no slip.

This matter of the formation of films has recently been investigated by Schutt and by Ramsden. The latter assumes that films are formed from material which is in the liquid, and which enters the film because in doing so it tends to minimize the energy of the film. It is apparent on this hypothesis that the smaller the bubble the thicker and more permanent the film would become. In addition, the slower motion of the small bubbles would be less likely to result in a tearing away of the film when once it was formed. An assumption of this kind accounts readily for the maximum and minimum values of the viscosity curve in olive oil, but it is not so evident that the curve would pass continuously between the two values. One would rather expect that there would be a point of discontinuity corresponding to the first formation of a permanent film.

This idea of a permanent film fits particularly well the results in linseed oil. Of all the oils used this one has the greatest film-forming power. Indeed, films may be formed on a wire loop and remain intact for twenty minutes in the open air. Correspondingly, we notice that there is no marked evidence of slip between the air and this oil, a result which would follow if the surface film remained intact even with large bubbles.

Among the liquids used aniline approaches most closely to linseed oil in its film-forming properties. It will be remembered that it was with aniline that Allen obtained such irregular results. Fig. 10 shows the results of observations

Fig. 10.



on an air bubble in this liquid. Both curves are irregular, but as a rule the low points of the velocity curve correspond to points on the  $r^2$  curves where the radius is diminishing most slowly. These results are easily explained on the assumption that a film forms with a great readiness in this liquid, but is also easily destroyed. The slow velocities and slight decrease in size correspond, then, to the existence of a film; the high velocities and faster decrease to the absence of a film. This explains how Allen could obtain some velocities so much larger than those computed on the assumption of no slip, and yet obtain others so nearly in agreement with the computed values.

Of the oils used, linseed oil and glycerine showed least evidence of surface slip; castor oil, colza oil, machine oil, cottonseed oil, and paraffin oil agreeing more nearly with olive oil in their behaviour. Since, however, the amount of slip is a function not only of the kind of oil but also of the size of the bubble, it would be meaningless to speak of the coefficient of slip of a particular oil. Our picture of the surface conditions which give rise to the appearance of slip would, indeed, lead us to predict that the slip at the surface of a sufficiently large bubble would appear infinite in any liquid.

*Radii of Molecular Attraction.*

It is interesting to consider the significance of the rate of diminution of the air bubbles. As has been stated, this is but slightly dependent upon the rate of diffusion of the air in the oil, but seems, on the contrary, to depend for the most part on the adhesion of a film of air to the oil surface. If this is the case, the film would be of a thickness proportional to the sphere of action of the oil molecules, and indeed would be expected to be to a first approximation equal to the radius of the sphere of action. It is easy to get an idea of the thickness of this film. We have seen that if we represent by  $x$  the distance traversed by the sphere,

$$dr^2/dx=c,$$

whence

$$2\pi r \frac{dr^2}{dx} = \frac{d(\frac{4}{3}\pi r^3)}{dx} = 2\pi rc.$$

This states that the diminution in volume is just sufficient to provide a lining of thickness  $c$  for the tube of radius  $r$  through which the sphere is moving. The value of  $c$  actually obtained from the curves is of the right magnitude to verify our assumptions, as will be seen from the following values:—

Olive oil .....	$3.6 \times 10^{-6}$
Colza oil .....	$8.5 \times 10^{-6}$
Castor oil .....	$10.0 \times 10^{-6}$ .

Although there are several factors whose omission prevents us from concluding that these values are actually the radii of molecular attraction in the different oils, the close agreement of these values with those ordinarily assigned from the results of utterly different types of experiments is quite remarkable. It may be that further experiments along this line will result in a method of determining at least the ratio of the spheres of attraction in some of the oils which are most amenable to this process.

*Summary.*

It is possible to make metallic spheres sufficiently small and uniform in density and in surface texture to allow of the verification of Stokes's law in the less viscous oils.

One of these spheres may be used instead of the capillary tube method to test the rate of variation of viscosity with temperature or with pressure, with probably greater accuracy, and certainly with greater ease and rapidity.

Ladenberg's correction for the effect of the walls of the fall tube is independent of the viscosity, and holds for spheres of radii not greater than one-tenth the radius of the tube.

Stokes's law, with the above correction, holds in the less viscous liquids to within at least one-half of one per cent.

The inertia terms begin to have an appreciable effect when the radius of the sphere is about six-tenths of the critical radius.

The coefficient of sliding friction at the surface of the solid spheres used is certainly greater than 5000, and probably greater than 50,000.

The theoretically derived formula involving the coefficient of sliding friction holds in the case of complete surface slip.

The slip at the surface of a bubble of gas rising through a liquid may be either approximately zero or infinite. This can be explained from the film-forming properties of the liquids, and hence we may explain the irregularities of previous experiments on the rise of air bubbles.

A consideration of the erosion at the surface of an air bubble leads to the possibility of a new method of determining the relative spheres of molecular attraction in liquids.

In conclusion the author wishes to express his thanks to Professor Michelson and the staff of the Ryerson Laboratory, and especially to Professor Millikan, at whose suggestion and with whose direct and inspiring supervision this work was carried out.

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LXXV. *The Mobility of the Positive Ion in Flames.* By S. G. LUSBY, M.A. (Sydney), Emmanuel College, Cambridge, Barker Graduate Scholar of the University of Sydney\*.

(1) *Introduction.*

THE determination of the mobilities of the ions produced when certain salt vapours are introduced into a Bunsen flame has occupied the attention of many experimenters since Arrhenius† first set this type of work on an exact basis. Most observers, however, have confined their attention to the negative ion, owing to the rapid growth of our knowledge of the negative electron. It has now been demonstrated beyond

\* Communicated by Sir J. J. Thomson.

† Arrhenius, Wied. *Ann.* 1891.

all doubt by Gold\* and H. A. Wilson† that in high temperature flames the negative ion is a pure electron. Within the last few years, however, the attention of physicists has been transferred to positive carriers of electricity. The present paper gives an account of some measurements made on the mobility of the positive ion in a Bunsen flame whose temperature could be varied within fairly wide limits. Observations were made at intervals of about  $200^{\circ}$  on all salts whose conductivity was high enough for accurate measurement.

The first determinations of the velocities of flame ions were made by H. A. Wilson‡, whose results may be summarised thus :—In a Bunsen flame at  $2000^{\circ}$  C. all salts of all metals of the alkali and the alkaline earth groups produce a positive ion whose mobility is 62, and a negative ion whose mobility is 1030 cm. a second under an electric force of 1 volt per centimetre; in hot air at  $1000^{\circ}$  C. positive ions of the former group have a mobility of 7.2, those of the latter group 3.8, whilst both groups give a negative ion whose mobility is 26. It is now known that these results are inaccurate owing to serious errors introduced in the determination of the potential gradient in the flame. In the negative measurements a uniform gradient was assumed, whilst in the positive measurements the gradient was plotted, but only in the pure flame, whereas the salt bead introduced in the experiment very appreciably alters the distribution of potential in the flame. An indirect determination of mobility was made by Marx§ from considerations of the potential gradient in a flame in which salt vapours were sprayed. In order to make his experiments amenable to mathematical treatment, Marx was obliged to assume that all the ionization took place in the flame, and none at the surface of the electrodes. The values of the positive mobility thus obtained were very variable, ranging from 120 to 340, with a doubtful mean of 250. This method is very interesting from the theoretical point of view, but is too indirect to give accurate results. The only other measurements which concern us are those of Moreau||, who simplified matters by assuming a uniform fall of potential in the flame, thus deducing a mobility of 80 at  $2000^{\circ}$  C. Thus all three of the results quoted suffer by reason of incorrect values given to the potential gradient in the flame. The order of the errors introduced is illustrated

\* Gold, Proc. Roy. Soc. lxxix. A. (1907).

† Wilson, Proc. Roy. Soc. lxxxii. A. (1909).

‡ Wilson, Phil. Trans. A. (1899).

§ Marx, *Ann. der Phys.* ii. p. 790 (1900).

|| Moreau, *Ann. de Chim. et Phys.* 1903.



by the following example; under certain conditions, the author found that in a pure flame the minimum gradient was 6.5 volts per cm., in a salted flame only 0.7, whilst an assumption of uniform gradient led to 22. The magnitude of the error will depend on the temperature of the flame; at temperatures below 1150° absolute it was found that the three cases quoted above would give similar results.

### (2) *Experimental Details.*

The method employed in the present series of measurements was that adopted by Wilson in 1899. Two electrodes are placed horizontally above one another in the flame, and the current between them is measured for different potential-differences—the upper plate being charged positively. A small bead of salt is then introduced into the flame just beneath the upper electrode, and the current measurements are repeated. When the potential-difference is great enough to drive back the positive ions against the uprush of the gas, the current suddenly increases. The exact potential required is obtained by comparing the two current curves. Knowing this critical voltage, one can obtain the *minimum* electric force in the flame; if then the upward velocity of the flame gas is known, a simple calculation gives the ionic mobility.

For a full account of the experimental arrangements reference must be made to a preliminary paper by the author\*. The alteration in temperature was effected in three ways:—(1) By altering the relative proportions of gas and air; (2) by raising or lowering the burner; and (3) by altering the mesh of the lower electrode. By combining these three devices it was found possible to secure a flame at temperatures ranging from 1150° to 1950° absolute.

### (3) *Account of Observations.*

At the very first temperature investigated, viz. 1450°, a search was made to see whether the mobility of the ions produced by the salts of a given metal depended on the particular salt used. Potassium was chosen, because its conductivity is high and its salts are easily procurable. The following salts were carefully tested:—

$K_2CO_3$ ; KOH; KCl; KBr; KI ..... Simple salts.

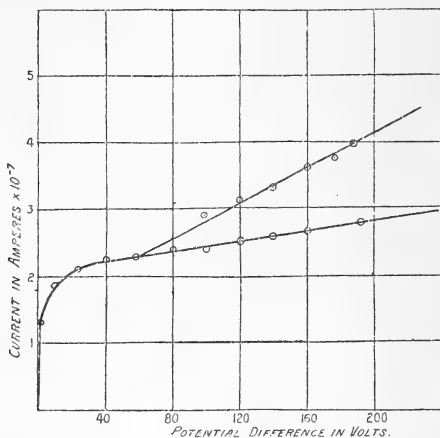
$K_2Mn_2O_8$ ;  $KNaCO_3$ ;  $K_2Fe(CN)_6$  ..... Complex salts.

Other salts, *e. g.* the nitrate, were tried, but had to be

\* Camb. Phil. Soc. xvii. 1, p. 26 (1910).

rejected on account of their extreme volatility. In no case were the variations in the critical voltage deduced from the current curves outside the limits of experimental error. A typical curve is shown in fig. 1, in which ordinates represent current and abscissæ the potential-difference between the electrodes.

Fig. 1.  
Current in Pure and Salted Flame.



A complete investigation of all the suitable salts of the conducting metals was then made, experiments being made at intervals of about  $200^{\circ}$ . The salts available for use at each temperature of course varied according to the temperature. As the temperature is reduced, the number of salts suitable for exact work diminishes, owing to the fact that the melting-points of many salts are above the flame temperature. On the other hand, many salts which at high temperatures are too volatile to employ prove very useful at low temperatures. At  $1150^{\circ}$  it was rather difficult to work with divalent metals (barium, strontium, and calcium) as their conductivity is so low; the chlorides of barium and strontium were the most reliable, whilst no calcium salt at all could be used. The only calcium salt that could be employed even at the highest temperature was the chloride; it was found necessary to dry it immediately before use. Thus for any generalization made about divalent metals there is not very strong direct evidence in the case of calcium. No trivalent salts could be found with conductivity high enough or volatility low enough for measurements of mobility. If one could be discovered, it would be possible to investigate the relation between valency and mobility at low temperatures.

Following is the list of the salts used:—

CsCl ; Cs <sub>2</sub> CO <sub>3</sub> ,	} Monovalent metals.
RbCl ; Rb <sub>2</sub> CO <sub>3</sub> ,	
KCl ; K <sub>2</sub> CO <sub>3</sub> , &c., see above,	
NaCl ; Na <sub>2</sub> CO <sub>3</sub> ; NaOH,	
LiBr ; Li <sub>2</sub> SO <sub>4</sub> ,	
BaCl <sub>2</sub> ; BaCO <sub>3</sub> ,	} Divalent metals.
SrCl <sub>2</sub> ; SrCO <sub>3</sub> ,	
CaCl <sub>2</sub> .	

It was found that from 1300° upwards all these salts produced ions of the same mobility; below 1300°, however, the monovalent metals led to a greater mobility.

#### (4) *Variation of Current with Temperature.*

The saturation current in the flame fell off very rapidly with the temperature, so that at low temperatures a very sensitive galvanometer was required. In the earlier work a d'Arsonval instrument giving 10<sup>8</sup> scale-divisions per ampere was employed; at low temperatures it was replaced by a Nalder instrument 15 times as sensitive. On account of the small distance between the electrodes (about 3 cm.) saturation is closely approached with a fairly small voltage. With 100 volts between the electrodes, the current generally attains three parts of its saturation value. As no figures connecting flame temperature with saturation current have yet been published, I give below in Table I. the mean values deduced from a large number of curves. No special attention was paid to this branch of the work, but it was thought desirable to put the results on record. The effective area of the electrodes was about 2 sq. cm.; the values given are for the total current.

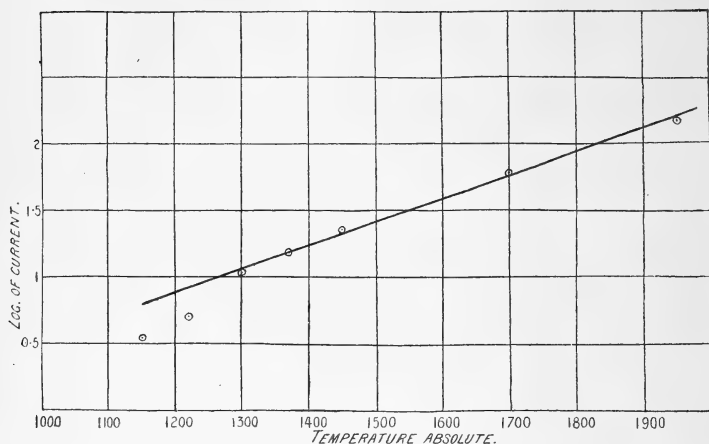
TABLE I.  
Saturation Current and Temperature in Pure Flame.

Temp. Abs.	Saturation Current.	Log. of Current.
1150°	35×10 <sup>-9</sup> amp.	54
1220	51	71
1300	107	103
1370	150	118
1450	230	136
1700	600	178
1950	1500	218

In fig. 2 the logarithms of the currents are plotted against the corresponding temperatures. It will be seen that the linear relation connecting these two coordinates is very close.

Fig. 2.

Current and Temperature.



This suggests that the current increases with the temperature according to an exponential law. The values for the current at the two lowest temperatures do not lie on the curve. This is due to the fact that these two values were obtained with a different cathode, whose mesh was finer than in the other case.

#### (5) *Determination of Potential Gradient.*

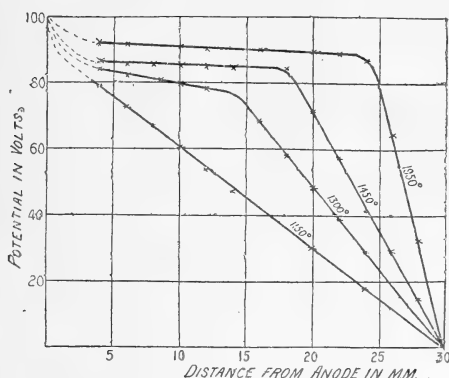
The minimum potential gradient in the flame was determined in the way indicated previously\*. In most cases a quadrant electrometer of low sensitiveness was used. A constant potential-difference was maintained between the quadrants, whilst the search-wire in the flame was joined to the needle. The instrument used gave deflexions directly proportional to the potential up to 120 volts.

The readings were remarkably constant for the salted flame, but not quite so good for the pure flame. The potential-difference applied between the two electrodes in the flame was that found experimentally (see fig. 1); it was the minimum required to drive back the positive ions against the flame gases.

\* Proc. Camb. Phil. Soc. i. p. 26 (1910).

The potential curves thus obtained for the salted flame exhibit three marked characteristics: (1) a small anode fall; (2) a region of small constant electric force (this is the quantity required for determination of mobility); and (3) a very sudden cathode drop. As the temperature is reduced, the following modifications occur:—(1) the anode fall increases slightly; (2) the region of constant electric force contracts, and the force itself increases; and (3) the cathode fall becomes less abrupt. Finally, when a temperature of  $1150^{\circ}$  is reached, the second and third branches of the curve merge into one straight line, but the anode fall persists. On account of the presence of the salt bead, no readings could be taken within less than 4 mm. of the anode. Thus it seems as if below  $1150^{\circ}$  one can regard the fall of potential in a hot gas as uniform. Wilson\* made this assumption in working with hot air at  $1270^{\circ}$ , in which case it is not quite true. Specimen results at four temperatures are plotted in fig. 3, in

Fig. 3.  
Fall of Potential in Salted Flame.



which ordinates represent potential and abscissæ distances from the anode. The results obtained at the other temperatures are intermediate in their characteristics, and are omitted to avoid crowding the curves. For convenience in plotting, all the curves have been reduced to a common potential-difference between the electrodes, viz. 100 volts, though it must be understood that the potential actually applied in each case was that just required to reverse the motion of the positive ions. The temperatures stated are the mean values for that part of the flame in which the minimum electric intensity

\* Wilson, Phil. Trans. A. 1899.

occurs. The temperatures were measured with a thermocouple whose members were platinum and platinum-rhodium. The couple was standardized by the melting-points of very small beads of various salts. The curves shown agree roughly with some given by Marx (*loc. cit.*), who sprayed salt vapours into his flame, and thus got an evenly distributed source of ionization, very different to the case in which a small salt bead is placed under the upper electrode. On account of this difference in the method of ionization, one would not expect very close agreement of Marx's curves with those of the author. Marx did not state the temperatures at which his curves were taken, but merely indicated the appearance of the electrodes—white-hot, red-hot, &c.

#### (6) *Velocity of the Flame Gases.*

The determination of the upward velocity of the gas was made from a comparison of the pressures of the air and the gas, and exact measurement of the volume of air used. For this purpose a water-gauge was used to determine the pressures of the gas and the air, or both combined, just before entering the burner; all three were read by a cathetometer. The flow of air was obtained from the rate of fall of the cylindrical holder which supplied it.

#### (7) *Results obtained.*

In Table II. below are collected the final results obtained

TABLE II.—Mobilities of Positive Ions.

(a) Monovalent metals. (b) Divalent metals.

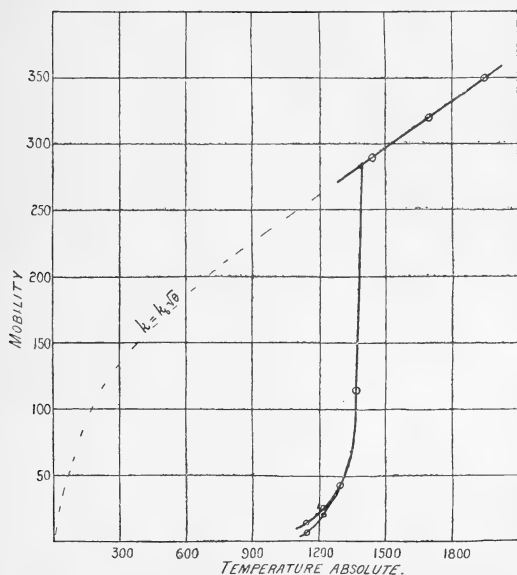
I.	II.	III.	IV.	V.	VI.
Temp. Abs.	Minimum Electric Force.	Gas Velocity.	Mobility.	Relative Mobility.	$k_0 \sqrt{\theta}$ .
1950°	0.61 volts/cm.	214 cm./sec.	350	100	100
1700	0.65	210	320	91.5	93
1450	0.71	206	290	83	86
1370	1.58	181	115	33	83.5
1300	3.87	164	42.5	12.1	81.5
1220	(a) 7.18	183	(a) 25.5	(a) 7.3	79
„	(b) 9.16		(b) 20.5	(b) 5.8	
1150	(a) 17.0	207	(a) 12.2	(a) 3.5	77
„	(b) 3.3		(b) 6.2	(b) 1.8	

at various temperatures. The temperature stated refers to the mean value for that portion of the flame in which the minimum gradient occurs. In the last column are given the relative mobilities on the assumption that the mobility varies as the square root of the temperature.

It will be seen by comparing columns V. and VI. that at the three highest temperatures given the mobility varies very approximately as the square root of the temperature. This, it will be shown later, denotes an ion of mass equal to that of a hydrogen atom between these limits of temperature. Below  $1450^{\circ}$  the mobility falls off very rapidly, until at  $1150^{\circ}$  it only retains a few per cent. of its former value. Had the law  $k=k_0\sqrt{\theta}$  persisted, the mobility at  $1150^{\circ}$  would have fallen to only 77 per cent. of the highest value. It is obvious that extensive clustering sets in at temperatures under  $1450^{\circ}$ . By representing the results graphically (*vide* fig. 4), it is

Fig. 4.

Variation of Mobility and Temperature.



seen that this clustering commences at about  $1400^{\circ}$ . Down to  $1300^{\circ}$  ions from all metals give the same result, but at the two temperatures examined below  $1300^{\circ}$  it was found that the ions produced by the divalent metals had a smaller

mobility than those produced by the monovalent metals. At  $1150^{\circ}$  the ratio of the two mobilities is very closely 2 to 1. This confirms a result obtained by H. A. Wilson quoted before, viz. that in hot air at  $1270^{\circ}$  monovalent metals gave an ion moving twice as quickly as that coming from divalent metals. A fuller discussion of results is given in the next two sections.

#### (8) *Structure of the Positive Ion Flame.*

In order to form some theory as to the nature of the ion we require to know its mass, or else its "electric atomic mass." This can be calculated approximately from the mobility by using Langevin's simple formula for the mobility  $k = \lambda e / mv$ , where the quantities have their usual significance. This formula involves the following assumptions:—(1) that the velocity of the ion due to the electric field is negligible in comparison with its thermal velocity of agitation; (2) that the ion comes to rest after each collision; and (3) that the charge of the ion does not affect its mean free path (as deduced from the kinetic theory of gases). In the present experiments the first assumption is amply justified. The second cannot be absolutely true, but we can form a rough idea as to the nature of the error involved. The question of the "persistence" of velocity of uncharged molecules after collision has been investigated by Jeans\*, who shows that, on the average, there is a tendency for a molecule to persist in moving along its original path after collision with 40 per cent. of its original velocity. If the colliding body is much smaller than the molecule, the persistence is only 33 per cent., if much larger 50 per cent. In general, the effect of this persistence of velocity is to *increase* the free path; *e. g.* as regards calculation of viscosity, this increase is 25 per cent. The order of this increase is much the same in all kinetic theory calculations. Now, coming to the third assumption, we find ourselves faced with corrections of a different order and a more doubtful nature. It was first shown by Langevin† that the effect of endowing a molecule of a gas with a charge is to *decrease* its free path; this decrease is due to the mutual induction between ion and molecule. It can be shown that if  $\lambda'$  is the free path of a charged molecule, and  $\lambda$  that of an uncharged molecule,

\* Jeans, 'Dynamical Theory of Gases,' p. 236.

† Langevin, *Ann. de Chim. et Phys.* vii. p. 28 (1903).



then

$$\frac{\lambda}{\lambda'} = 1 + \frac{M_1}{M_2},$$

where  $M_1$  = mutual potential energy of ion and molecule at collision,

$M_2$  = kinetic energy of molecule.

Langevin shows that  $M_1 = \frac{K-1}{8\pi n} \cdot \frac{e^2}{r^4},$

where  $K$  = specific inductive capacity of the gas,

$n$  = number of molecules per c.c.,

$r$  = distance apart of ion and molecule at collision.

The difficulty in applying this correction is the uncertainty as to the value of  $r$ ; since  $M_1$  varies as the fourth power of  $r$ , any error in the value of  $r$  is quadrupled in the result. To illustrate the matter, let us take the case of air at normal pressure and temperature. We find that  $M_1/M_2 = 3.3$  if the ion is a single molecule, *i. e.* if the distance apart at collision is put equal to one molecular diameter. In this case electric attraction decreases the free path 4.3 times. If, however, the ion consists of a single layer of molecules grouped round a central molecule, *i. e.*  $(2\pi + 1)$  molecules in all, the value of  $M_1$  is reduced 16 times, and is only 0.2; so that the free path is reduced only 20 per cent. If we calculate the mobility in each case, we find it approximately the same for both. In the first case the mobility

$$k_1 = \frac{e}{mv} \left( \frac{\lambda}{4.3} \right),$$

and in the second case

$$k_2 = \frac{\lambda e}{v} \left( \frac{1}{5m} \right),$$

the slight change in the ratio  $(\lambda/v)$  due to the size of the cluster being of a much smaller order than the other correction. This ambiguity in the interpretation of mobility experiments seems inevitable. A single molecule ion has its free path diminished by electric induction to such an extent that it behaves like a cluster ion which, on account of its large size, is scarcely affected by induction. Wellisch\* has interpreted his mobility experiments as supporting the idea that the ion is a single molecule. At ordinary temperatures the agreement between experiment and such a theory is very

\* Wellisch, Phil. Trans. A. (1909).

fair in the case of many gases ; but an examination of the law connecting mobility and temperature seems to decide in favour of the cluster theory. If the ion is a single molecule, then its mobility varies as  $\lambda/v$ , i. e. as the square root of the temperature ; this change will be slightly complicated by the change in  $M_1/M_2$ , which, as is shown below, decreases directly as the temperature. The general effect would be that the mobility would increase at a rate somewhat quicker than the square root of the temperature. The experiments of Phillips\*, however, show that between very wide limits of temperature the mobility increases directly as the temperature. These results help us to decide the ambiguity as to the nature of the ion in favour of a cluster.

At the temperature of flame experiments the effect of electric induction is extremely small even for a single molecule ion. It is seen that  $M_1$  is independent of temperature, since  $(K-1)$  and  $n$  vary in the same way ; and as  $M_2$  varies directly as the temperature, therefore the ratio of  $M_1/M_2$  decreases directly as the temperature increases. For air at  $0^\circ$ ,  $M_1/M_2=3.3$ , for air at  $2000^\circ$ ,  $M_1/M_2=0.4$  ; that is, the free path of a molecule would be *decreased* about 40 per cent. This effect would be annulled by that due to persistence of velocity, which, as we have shown, makes the free path *increase* about 25 per cent.

To sum up our discussion as to the fundamental assumptions involved in equating the mobility of an ion to  $\lambda e/mv$  at flame temperature, we conclude that the error is at the most only about 25 per cent., and is most probably far less.

We have now to substitute in this formula the values of  $r$  and  $v$  proper to a foreign body moving amongst the molecules of a given gas. If the mass of the foreign body, i. e. the ion, is  $m_1$ , the mass of a molecule  $m_2$ , and the number of molecules per c.c. is  $n_2$ , then the free path of the foreign body ( $\lambda_1$ ) is given by

$$\lambda_1^{-1} = \pi n_2^2 \left( \frac{\sigma_1 + \sigma_2}{2} \right)^2 \cdot \sqrt{1 + \frac{m_1}{m_2}},$$

where  $\sigma_1$  = diameter of the ion,

$\sigma_2 =$  „ „ molecule.

Putting  $\frac{m_1}{m_2} = x$  and  $\frac{\sigma_1}{\sigma_2} = y$ ,

\* Phillips, Proc. Roy. Soc. A. lxxviii. (1906).

this becomes

$$\lambda_1^{-1} = \lambda_2^{-1} \cdot \left( \frac{1+y}{2} \right)^2 \cdot \sqrt{\frac{1+x}{2}},$$

where  $\lambda_2$  is the mean free path of a gas molecule, and  $\lambda_2^{-1} = \pi \cdot \sqrt{2} n_2 \sigma_2^2$ .

Also an assumption of equipartition of energy gives

$$m_1 v_1^2 = m_2 v_2^2;$$

whence finally the mobility

$$\begin{aligned} K_1 &= \frac{\lambda_2 e}{m_2 v_2} \left( \frac{2}{1+y} \right)^2 \cdot \sqrt{\frac{2}{x(1+x)}} \\ &= K_2 \cdot \psi(y) \cdot \phi(x). \end{aligned}$$

In this result suffix 2 refers to the molecule, whilst the two factors  $\psi(y)$  and  $\phi(x)$  give the corrections due to the size and mass of the ion being different to those of the molecule. If we knew in general terms the relation between the size and the mass of a molecule, we could solve this equation directly and find the mass of an ion as soon as we knew its mobility. In the absence of such knowledge we are driven to make tentative solutions. As the flame gases are mostly air, we shall assume the kinetic constants of air in our solutions. Taking the result obtained at  $1950^\circ$ , viz. a mobility of 350, such a high mobility suggests a very small ion, so we make a tentative solution of the mobility of a charged atom of hydrogen. The following data are used:—

$$\left. \begin{aligned} \lambda_2 &= 69 \times 10^{-6} \text{ cm.} \\ v_2 &= 12 \times 10^4 \text{ cm./sec.} \end{aligned} \right\} \text{ at } 1950^\circ \text{ abs.}$$

$$\frac{e}{m_2} = \frac{3 \times 10^{14}}{29} \text{ in E.S. units.}$$

$$x = \frac{1}{2.9}; \quad \phi(x) = 7.48.$$

$$y = 0.35; \quad \psi(y) = 2.20.$$

Whence the mobility  $K_1 = 320$  cm. a second. The experimental value obtained is so close to this that one concludes that at  $1950^\circ$  the positive ion either is, or else has the same mass as, an atom of hydrogen. Further, according to the formula proposed, the mobility should vary as  $\lambda/v$ , i. e. as the square root of the temperature. A reference to the results (Table II., columns V. and VI.) shows that this relation actually does hold true very closely between  $1950^\circ$

and  $1450^{\circ}$ . Thus it appears that at high temperatures the mass of the positive ion remains unaltered, and is equal to that of a hydrogen atom. Below  $1400^{\circ}$  the mean size of the ion increases rapidly. Let us assume that  $\phi(x)$  and  $\psi(y)$  are equal to unity, i. e. that the ion is one molecule. We find, on solution, that an ion of specific mass 36 has a mobility of 12.2, which is the value obtained at  $1150^{\circ}$ . Within the limits of error this might represent a molecule of either nitrogen or oxygen—both of which are present in the flame, or else a molecule of carbon dioxide, or two molecules of water vapour—these being the two main products of combustion. Probably ions of all these types are present. The most obvious way of accounting for the decrease in mobility is to suppose that clustering commences round the high temperature ion as nucleus. At moderately high temperatures only a few such clusters exist, on the average, at any instant; but as the temperature falls the number of clusters increases until we reach the stage noted at  $1150^{\circ}$  when every ion is a single molecule. At any intermediate temperature we should have some simple ions and some clusters; e. g. at  $1300^{\circ}$  the mobility is only 42, which means that approximately six ions out of every seven consist of a single molecule (see Table II., columns V. and VI.). Thus at any such temperature we must imagine a constant combination and dissociation between the high temperature ion and a molecule. If the simple ion is actually a charged atom of hydrogen, this may be conceivable; if not, we have to explain how the positive charge can leave one body and transfer itself to another. The question will be touched on later in more detail.

As the temperature falls still lower, we know from the experiments of Moreau\* and McClelland† that the size of the ionic cluster increases very rapidly—in fact, as the fifth power of the temperature. If we take McClelland's highest result—a mobility of 0.23 at  $500^{\circ}$ —and the author's lowest result—a mobility of 12 at  $1150^{\circ}$ —this fifth-power law fits in very well. This law of temperature change is very different from that found by Phillips (*loc. cit.*) for ions produced by Röntgen rays in gases, in which case the mobility varies directly as the temperature. The tendency to cluster is far stronger in flame gases than in ordinary pure gases. This is probably due to the products of combustion; for de Broglie‡ has shown that if a flame produces condensable products of

\* Moreau, *Ann. de Chim. et Phys.* 1906.

† McClelland, *Phil. Mag.* July 1898.

‡ de Broglie, *Journ. de Phys.* Dec. 1909.

combustion, large neutral bodies are formed which combine with extreme rapidity with small ions; if no condensable products are formed, there is no tendency to cluster.

Besides the well-known electropositive nature of hydrogen in the electrolysis of solutions, there is a certain amount of experimental evidence supporting the view that the high temperature ion is actually an atom of hydrogen. The strong tendency of hydrogen to carry a positive charge is exhibited by some experiments on the positive discharge from sodium phosphate made by Horton \*. It was found that on introducing hydrogen into the exhausted discharge-tube, the positive current was increased 80 times. Carbon monoxide (which on other grounds Horton considers to be the positive carrier in his experiments) only increased the current 7 times. Garrett † measured the mass of the positive carrier from aluminium phosphate, and found it to be that of an atom of hydrogen. Richardson ‡ discovered that in the case of heated platinum a large amount of hydrogen escapes in the form of positive ions. His later experiments, which consistently reveal a positive carrier of specific mass about 30, seem to indicate that these charged atoms (or molecules) of hydrogen have a very strong tendency to combine with some larger molecule. The only other case in which the positive carrier has been investigated is that of canal rays. Here again a particle of unit mass always occurs, no matter what may be the gas experimented on; in addition to this particle, the atoms of the gas occur with a positive charge. On the whole, it seems most probable that the small positive carrier which so often occurs is actually an atom of hydrogen. As hydrogen is present in the flame, there is no difficulty in explaining the source of the positive carrier; how to explain the method by which the hydrogen atoms acquire their charge is more doubtful.

It has been suggested frequently that ionization in a flame is brought about by chemical action induced by high temperature. In a recent paper Bloch § has examined a number of low-temperature flames (the so-called "phosphorescence" of sulphur, phosphorus, &c.), and found that, with the sole exception of phosphorus, chemical action is not accompanied by ionization. It is, of course, quite possible that at higher temperatures chemical action is so intense that ionization is produced by mechanical rupture of the surface

\* Horton, *Camb. Phil. Soc.* xvi. p. 1 (1910).

† Garrett, *Phil. Mag.* Oct. 1910.

‡ Richardson, *Phil. Trans. A.* p. 207 (1906).

§ Bloch, *Ann. de Chim. et Phys.* April 1911.

of the molecules. An alternative method of ionization that may be suggested is that when the metallic salts are introduced into the flame they expel electrons which ionize by impact. If, however, these electrons are in equilibrium with the molecules of the flame gases, ionization by impact does not appear to be possible. The equivalent potential fall of an electron in temperature equilibrium may be deduced from the energy relation  $Ve = \frac{1}{2}mv^2$ . At  $2000^\circ$  we find that  $V$  is only 0.25 volt. At ordinary temperatures a potential drop of at least 5 volts is necessary for ionization by impact. Thus it appears that in a flame the electrons cannot ionize by impact unless either their velocity exceeds the equilibrium value, or else the energy required for ionization is much less than at normal temperatures. These two points can only be settled by further experiments.

The simplest conceivable type of ionization would be the separation of the metal salt into two ions, a positive metal ion and a negative acid radicle. That positively charged metal atoms exist in the flame seems fairly certain; for Lenard has shown that the salt vapour which exhibits the characteristic coloration in the flame is positively charged. It has, however, been established that the coloration of a flame is quite independent of its ionization\*. For instance, if chloroform be sprayed into a salted flame, the coloration disappears, but the conductivity is scarcely affected. These two facts suggest very strongly that besides the metal ions (which cause the characteristic colour), some smaller ions are present which produce the conductivity of the flame: all observers agree that the salts of all alkali metals produce an ion of the same mobility; lithium with an atomic mass of 7, for example, produces a similar ion to caesium whose atomic mass is 133. Professor Wilson† has recently made an attempt to explain this by supposing that the ions are really metal atoms, but that the charged life of the ion increases with the atomic mass of the metal. To get the apparent constancy of mobility that is observed, one must assume that the charged life of the atom varies as the square root of its mass. The experimental test that Professor Wilson has deduced for this law leads to values of the "true" mobility which are three times greater than those deduced from the equation  $k = \lambda e/mv$ ; such a discrepancy seems too large to justify the law suggested. Franck and Pringsheim‡ have recently examined a flame consisting of hydrogen and chlorine.

\* Smithells, Wilson, and Dawson, *Proc. Roy. Soc.* lxiv. 1898.

† H. A. Wilson, *Phil. Mag.* June 1911.

‡ Franck and Pringsheim, *Deutsch. Phys. Ges.* xiii. p. 8 (1911).

They found that if a salt bead were introduced, the negative ions were much larger than the positive. On account of the strong attraction of the chlorine atoms for electrons, the negative ions were atoms of chlorine, the positive ions being most probably the hydrogen atoms. The exact mobilities could not be determined; but it was found that the positive ion had less than one-tenth the mass of the negative ion, *i. e.* the chlorine atom. All the experimental evidence at our disposal leads one to imagine that the positive flame ion, though primarily due to the metal salt, is not an atom of the metal, but some smaller body that is always present in the flame.

*Summary.*

(1) The mobility of the positive ion due to salt vapours in a Bunsen flame has been measured at intervals of temperature ranging between  $1150^{\circ}$  and  $1950^{\circ}$  absolute.

(2) Down to  $1300^{\circ}$  all salts of all conducting metals produce the same ion; below this temperature the ion due to monovalent metals has a greater mobility than that due to divalent metals.

(3) Between  $1950^{\circ}$  and  $1400^{\circ}$  the mobility varies as the square root of the temperature, and corresponds closely to that calculated for a hydrogen atom. Below  $1400^{\circ}$  the mobility drops very rapidly, as if extensive clustering took place.

In conclusion I desire to express my thanks to Professor Sir J. J. Thomson for his encouragement and advice during the course of these experiments.

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LXXVI. *The Mobility of Positive Ions produced from Heated Aluminium Phosphate in Gases at Low Pressures.* By GEORGE W. TODD, M.Sc., B.A., 1851 Exhibition Scholar of Birmingham University; Emmanuel College, Cambridge\*.

*Introduction.*

AT the present time, when practically all phenomena connected with the passage of electricity through gases can be explained by the presence of ions, any experiments which bring to light new properties concerning ions are valuable. Most of what is known of the structure of ions has been obtained from determinations of their mobilities. The present paper is concerned with the mobilities of the positive ions in gases at low pressures. Over

\* Communicated by Sir J. J. Thomson, F.R.S.

a wide range of pressures Rutherford\*, Langevin†, and Wellisch‡ have shown that the product of pressure and mobility is constant for a particular gas. Langevin took observations down to a pressure of 7.5 cm. of mercury, and found in the case of the negative ions in air and carbon dioxide when the pressure was below 20 cm., that the product of pressure and mobility increased rapidly with diminution of pressure, while in the case of the positive ions there was only a tendency to increase. Kovarik§ has determined the mobilities of the negative ions in air and carbon dioxide down to pressures of 1 cm., and he finds that the product of the pressure and mobility continues to increase very rapidly.

The writer has shown|| that the mobility of the *positive* ions produced by means of X-rays in gases at low pressures obeys the inverse pressure law down to a few millimetres of mercury. The experiments could not be carried further owing to the fact that the ionization produced by X-rays becomes very feeble at low pressures.

From his experiments, Langevin came to the conclusion that the abnormal increase in the mobility at low pressures was due to the dissociation of groups of molecules, of which he considered the ion to consist at higher pressures. There is evidence also, at any rate for the negative ion, for the view that the ion consists of a single molecule with a corpuscle attached, and that the latter at low pressures is continually migrating from one molecule to another, thus existing for a fraction of time in the free state.

It would be interesting to see whether the positive ion behaves in a manner similar to the negative ion at low pressures. The difficulty in such an investigation is in obtaining a sufficient number of ions to work with at low pressures. It is well known, however, that certain salts when strongly heated yield a copious supply of positive electricity, and this fact solved the difficulty. The experiments described in the paper last quoted were continued, using as a source of positive ions strongly heated aluminium phosphate—an especially good salt for the purpose—with the object of measuring mobilities at much lower pressures.

\* Camb. Phil. Soc. Proc. ix. p. 410.

† *Annales de Chimie*, vii. p. 28 (1903).

‡ Phil. Trans. A. cxix. p. 249.

§ Phys. Rev. xxx. 4, p. 420.

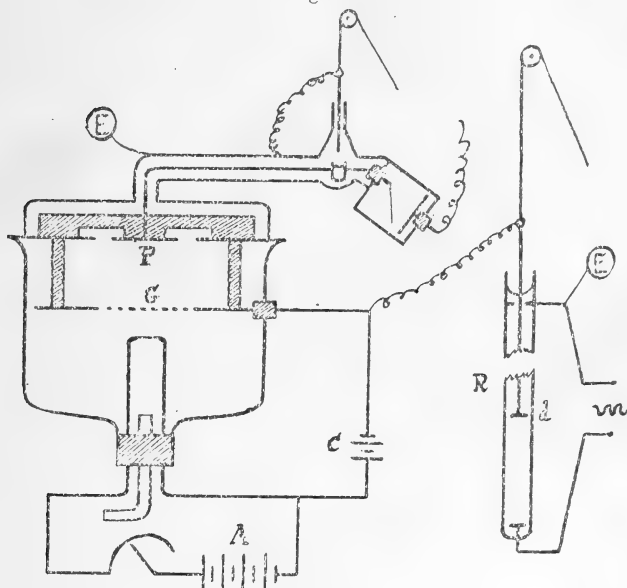
|| Camb. Phil. Soc. Proc. xvi. p. 21.



*Apparatus and Method.*

A diagrammatical representation of the apparatus is shown in fig. 1. P was a carefully insulated metal plate surrounded by a guard-ring and connected to a tilted electroscope. At a distance of 5.0 cm. below P and parallel to it was a metal gauze G which could be connected to a source of alternating potential, of which the maximum could be altered as desired by means of the potentiometer arrangement at R. This was

Fig. 1.



a copper sulphate resistance with its ends connected to the terminals of the alternating circuit, one of which was earthed. In most of the observations this alternating circuit was obtained from the town mains, but in some of the later observations the alternations of the field were produced by means of a rotating commutator which will be described later. By moving the copper disk *d* up or down in the solution, varying alternating potentials were tapped off for the gauze G. About a centimetre below the metal gauze were two thin strips of platinum on which aluminium phosphate had been deposited. These strips of platinum could be heated to a desired temperature by passing a current through them from an insulated battery of accumulators A, which was connected to the positive terminal of the cells C, so that the strips were always at a constant positive potential above the gauze G.

Thus when the platinum was heated a constant stream of positive ions was directed to the gauze and into the alternating field between it and the electroscope plate P.

If  $u$  = velocity of the ion per volt per centimetre, and  $d$  = distance between the gauze and the electroscope plate, then, if at any instant the gauze is at a potential  $E$ , the velocity of the ion at that instant will be  $uE/d$ .

Let the potential  $E = \phi(t)$  where  $\phi(t)$  is a periodic function of the time.

For an ion to reach the electroscope plate we must have

$$d = \frac{u}{d} \int_0^{\frac{T}{2}} \phi(t) \cdot dt,$$

where  $T$  is the period of alternation of the electric field.

In most of the experiments  $E = E_0 \sin 2\pi \frac{t}{T}$ ;

$$\text{hence} \quad d = \frac{u E_0 T}{d \pi}$$

$$\text{or} \quad u = \frac{\pi d^2}{E_0 T}.$$

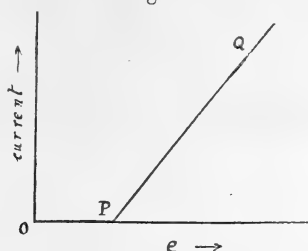
The voltmeter gives the "effective" value  $e$  of the alternating potential, hence, if the instantaneous value  $E = E_0 \sin pt$ , then  $E_0 = \sqrt{2} \cdot e$ . No correction was made for induction between the plates, the correction amounting to less than one per cent. The distance between the electroscope plate and the gauze was  $d = 5.0$  cm., and the number of alternations per second was 90, so that the mobility is given by

$$u = \frac{5010}{e}.$$

In making a determination of the mobility the pressure was brought down to required dimensions by means of a mercury pump and read on a McLeod gauge. The electroscope was then insulated and the alternating potential switched on. If this potential was more than sufficient to make the ions getting through the gauze travel the distance  $d$  in  $T/2$  the leaf would move across the scale of the electroscope. With the maximum alternating potential less than a certain critical value there would be no charge communicated to the electroscope. At each pressure a curve was drawn showing the relation between the current communicated to the electroscope and the effective value  $e$  of the alternating potential, and where this curve cut the axis ( $P$ , fig. 2) gave

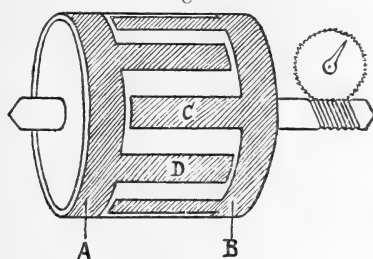
the critical value of  $e$  from which the mobility for that pressure was determined.

Fig. 2.



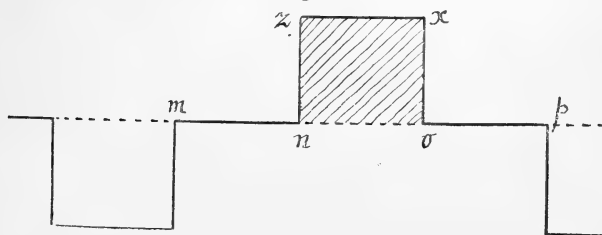
In some later experiments the alternating field was produced by means of the commutator shown in fig. 3. The shaded portions represent metal and the unshaded portions insulation. Brushes in contact at A and B were connected to an insulated source of potential. Two more brushes were placed at C and D at a distance apart equal to that between the centres of consecutive metal strips, so that when A was in

Fig. 3.



connexion with C, B would be in connexion with D. One of these, say C, was connected to earth and the other, D, to the potentiometer R (fig. 1), the other end of the latter being earthed. The commutator was driven by an electric motor and the speed regulated by adjusting the gear and current. Such an arrangement gave a curve of potential thus (fig. 4) :—

Fig. 4.



The points  $m, n, o, p$  were equidistant.

It has been shown that for an ion just to reach the plate of the electroscope

$$d = \frac{u}{d} \int_0^{\frac{T}{2}} \phi(t) \cdot dt$$

$$= \frac{u}{d} \left[ \text{area } n \circ x z \right],$$

see shaded portion above,

$$= \frac{u}{d} E_0 \frac{T}{4}$$

$$= \frac{u E_0}{4nd},$$

where  $n$  is the number of alternations per second,

$$\therefore u = \frac{4nd^2}{E_0} = \frac{100n}{E_0}.$$

The mobility was obtained in the usual way by plotting the current to the electroscope and the maximum alternating potential, while the number of revolutions of the commutator per second was maintained constant. The rate of rotation was tested before and after every reading with a stopwatch. With this commutator one could obtain up to 450 alternations per second.

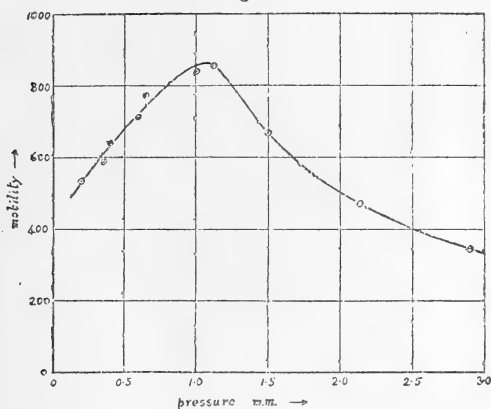
### *Experiments.*

There was no difficulty in making observations at much lower pressures than in former experiments. The stream of positive ions could be regulated by altering the heating current through the platinum strips to give any convenient rate of deflexion of the electroscope leaf in any gas. Using the town mains as the source of alternating potential mobilities up to five or six thousand centimetres per second could be measured, and with the more rapid alternations produced by the commutator one could measure mobilities of fifty thousand centimetres per second. As the electroscope plate required about 0.1 volt to carry the leaf across the timed portion of the scale, readings were not taken with alternating potentials having a maximum of less than one volt. A further limit was imposed on the observations by the increase in the mean free path with diminution of pressure. When the distance between the plates was less than about fifty free paths, readings were not taken.

In the first experiments a curious result was found. As the pressure was lowered the mobilities increased inversely as the pressure until about one millimetre was reached. At this

point the mobility of the ion reached a maximum value and then continued to fall gradually as the pressure diminished. The position of this maximum varied in different gases and slightly in the same gas. It was found later that this fall in mobility was due to the presence of water vapour. When great care was taken to dry the gas by allowing it to stand over phosphorus pentoxide for several days, and when the pressure in the apparatus before the introduction of this dry gas had been kept below 0.001 mm. of mercury by means of a charcoal tube and liquid air for some hours, it was found that the mobility continued to increase and at a greater rate than the inverse pressure law requires. Fig. 5 is a curve

Fig. 5.



showing the relation between the mobility and pressure for air when water vapour is present. The pressure at which the mobility begins to fall is in the same region as that in which the product of the pressure and the mobility begins to increase for the dry gas.

At ordinary pressures water vapour has practically no effect on the velocity of the positive ion, while it invariably retards the negative ion.

When the pressure was in the neighbourhood of 0.1 mm., it was noticed that ionization by collision of the positive ions took place if the maximum alternating potential was sufficiently great. The negative ions produced having presumably much bigger mobilities reached the electroscope plate in greater numbers than the positive ions, thus giving a negative charge to the leaf, so that the curve OPQ (fig. 2) would suddenly bend over at Q and cross the axis of potential. The effect diminished and disappeared as the free path arrived at dimensions comparable with the distance between the plates.

The results of the experiments with carefully dried gases are given in the following tables. Those marked \* were obtained with the commutator.

## Air.

Pressure.	Mobility.	Product.
8.8 mm.	113	99
6.00	170	102
4.38	231	101
3.02	334	101
1.20	876	105
1.13	918	104
.875	1715	150
.600	3830	230
.572	4220	242
* .540	6810	368
.452	7520	340
* .360	10800	389
* .200	17500	350
* .155	30200	467
* .150	47600	714
* .120	74100	890
* .120	68600	822
* .115	67800	780

CO<sub>2</sub>.

Pressure.	Mobility.	Product.
5.15 mm.	146	74.7
2.43	319	77.3
1.30	651	84.6
.99	895	88.8
.750	1280	96.5
.600	2640	158
.482	4190	203
* .410	5060	207
.393	6590	258
* .235	9810	231
* .190	27200	515
* .145	25600	371
* .120	51800	621
* .103	71900	741

CH<sub>4</sub>.

Pressure.	Mobility.	Product.
4.31 mm.	326	141
3.60	384	138
2.78	524	146
2.20	709	156
1.80	900	162
1.55	1310	202
1.25	2470	310
.975	3980	388
.820	5710	471

SO<sub>2</sub>.

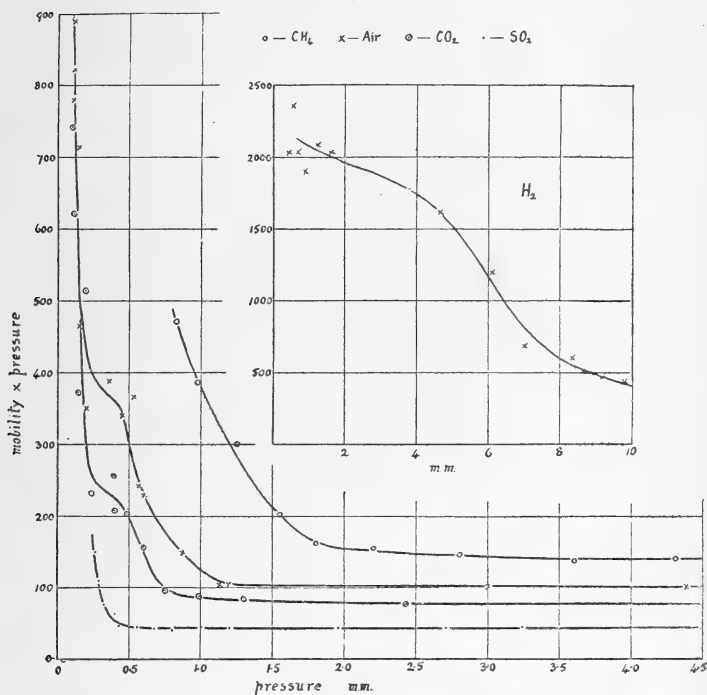
Pressure.	Mobility.	Product.
3.24 mm.	138	44.6
2.71	157	42.4
1.96	219	43.0
1.20	357	42.8
1.02	440	44.9
.820	487	39.9
.675	621	42.0
.562	781	44.0
.428	1094	46.9
.408	1540	63.1
.320	2450	78.3
.280	4005	110.2
.262	5720	150

H<sub>2</sub>.

Pressure.	Mobility.	Product.
12.2 mm.	330	403
9.80	449	440
8.35	729	605
7.05	978	690
6.10	1970	1200
4.65	3480	1620
* 1.63	14100	2300
* 1.25	19200	2400
* .860	21800	1890
* .700	29100	2040
* .540	43700	2360
* .450	45200	2030
* .400	86700?	3470?

The curves showing the relation between the pressure and the product of the pressure and mobility for the various gases are shown in fig. 6. It will be noticed that the pressure at which the product begins to increase rapidly is approximately inversely as the density of the gas.

Fig. 6.



The values for the mobilities at the higher pressures are practically the same as for the ions produced by X-rays, indicating that the particles which are ejected by the aluminium phosphate transfer their charges on collision to the gas molecules. In the author's previous paper on this subject the product of the pressure and mobility for hydrogen was rather low, and did not increase in the same region of pressure as it has been found to do in the present experiments. This was due to the fact that no care was taken to use dry and pure gas in the former experiments.

Some experiments were made to see whether the mobility depended on the rate of alternation of the field. It might

be possible that the positively charged particle emitted by the heated phosphate required a finite time for the ionic cluster to form round it. In that case, as soon as this finite time became comparable with the time taken by the ion to travel between the plates, the mobility would show an abnormal increase. Typical results with air at pressures above and below that at which the mobilities begin their abnormal increase, are given in the following tables. The mobility did not depend on the rate of alternation of the field.

Pressure = 1.585 mm.

Rate of alternation ( $n$ ).	Critical potential ( $E_0$ ).	Mobility.
25	3.88	644
38	5.37	708
41	6.01	681
86	13.6	630
115	17.5	658
169	25.4	665

Pressure = .742 mm.

$n$ .	$E_0$ .	$u$ .
96	3.82	2520
111	4.82	2280
149	6.35	2350
180	8.16	2210
204	8.20	2490

The results of the experiments point to some change in the structure of the positive ion at low pressures. It may be (*a*) that the ion is a cluster of molecules which eventually breaks up into a single charged molecule, or (*b*) that there is a positive unit smaller than the molecule which at low pressures is able to migrate from one cluster of molecules to another. It is interesting with regard to (*b*) that Lusby \*

\* Camb. Phil. Soc. xvi. p. 26.



has shown that the carrier of the positive current in flames above a certain critical temperature is independent of the salt introduced into the flame and the flame-gases, and is of the mass of a hydrogen atom, while below the critical temperature the carrier is much more massive, and depends on the salts used in the flame.

*Size of the Ion.*—Langevin has deduced from the kinetic theory of gases the formula for the mobility of an ion  $k = e\lambda/mv$ . It would be interesting to calculate the approximate values of the masses of the ions in the various gases using this expression, and to compare them with the masses of the molecules. In the expression for the mobility  $\lambda$  and  $v$  represent the mean free path and the velocity of thermal agitation of the ion. The mean free path of a molecule in a gas in which there are  $n_2$  molecules per unit volume, each having a diameter  $\rho_2$ , is given by

$$\lambda_2^{-1} = \pi \rho_2 n_2 \sqrt{2}.$$

The mean free path of an ion of mass  $m_1$  in the gas whose molecules have, say, mass  $m_2$ , is given by

$$\lambda_1^{-1} = \pi \frac{\rho_1 + \rho_2}{2} n_2 \sqrt{\frac{m_1 + m_2}{m_2}},$$

where  $\rho_1$  is the diameter of the ion. Hence the ratio  $\lambda/v$  for the molecule to that of the ion is

$$\frac{1}{2} \frac{\rho_1 + \rho_2}{\rho_2} \sqrt{\frac{m_1 + m_2}{2m_2}} \cdot \frac{v_1}{v_2} = \frac{1}{2} \frac{\rho_1 + \rho_2}{\rho_2} \sqrt{\frac{m_1 + m_2}{2m_1}},$$

since  $m_1 v_1^2 = m_2 v_2^2$ . The relations between the mass and diameter for the ion and molecule are not known, so that a definite value cannot be given to this ratio; but the trial of probable values will show that for an approximation no very grave error will be committed in assuming it to be unity. In the following table (p. 802) the mass of the ion has been obtained from  $k = e\lambda/mv$ , assuming the ratio  $\lambda/v$  to be the same for the ion and molecule.

Calculating  $m$  from the formula  $k = e\lambda/mv$ , it appears that the ion at ordinary pressures consists of a group of several molecules round the positive charge, and at very low pressures the group dissociates into a less complex group.

In the cases of air, carbon dioxide, and hydrogen, the experiments were carried out to as low a pressure as possible. There is a suggestion of a flattening in the air-curve when

the product of pressure and mobility has a value of about 360, and the same thing occurs in the case of carbon dioxide at approximately 240. If these bends in the curve are real,

Gas.	Mass of molecule $\times 10^{24}$ .	$\lambda(0^\circ \text{ \& } 760)$ $\times 10^8$ .	$v(0^\circ)$ .	$m \times 10^{24}$ .	
				Ordinary press.	Lowest press.
H <sub>2</sub> .....	2	1780	169800	25 (12 mols.)	5 ( 2 mols.)
CH <sub>4</sub> ...	16	800	60000	96 ( 6 „ )	29 ( 2 „ )
Air .....	29	960	44700	216 ( 7 „ )	24 (<1 „ )
CO <sub>2</sub> ...	44	650	36100	243 ( 5 „ )	25 (<1 „ )
SO <sub>2</sub> .....	64	470	29800	361 ( 6 „ )	107 ( 2 „ )

it means that the ion at that stage of its dissociation becomes very stable, and resists disintegration until the pressure is lowered further. This stage in both air and carbon dioxide corresponds to an ion consisting of about two molecules.

In the case of hydrogen the product of pressure and mobility remains fairly constant between 4.0 mm. and 0.5 mm. pressure, and it could not be ascertained whether the mobility increased again at lower pressures because the limit of the apparatus had been reached. This stage in hydrogen also corresponds to about two molecules to the ion.

*Note on the Carriers of the Positive Charge  
from Hot Salts.*

Although several experiments have been made to determine what actually is the carrier of the positive charge, the question is still uncertain. Sir J. J. Thomson \*, who first measured the ratio  $e/m$  for the positive particles from an iron wire and a carbon filament, found that  $m$  was about 26 times the hydrogen atom, and he suggested that the carrier might be the molecule of carbon monoxide, because the spectrum of a discharge in the tube gave the carbon-monoxide lines. Richardson † has shown that the mass of the positive carrier from heated metals is independent of the metal, and is the same as that found by Sir J. J. Thomson. He suggested that the carrier was a common impurity in all

\* 'Conduction in Gases,' 1906, p. 148.

† Phil. Mag. xvi. p. 740 (1908).

the metals used, and was probably the atom of sodium. The spectroscopic work of Horton\* points to carbon monoxide as the carrier, while Garrett†, from measurements of  $e/m$ , finds positive particles as small as the hydrogen atom.

In some experiments on the positive leak in different gases, Horton‡ has found that carbon monoxide has a great affinity for the positive electricity from a heated phosphate, so that when carbon monoxide is present in a gas the positive leak is practically wholly carried by the carbon-monoxide molecules.

It is well known that the carbon-monoxide spectrum is invariably visible in a discharge-tube. Heating the tube or prolonging the time of discharge makes the spectrum more pronounced. In his experiments on the variation of the positive leak from metals with the pressure, Richardson§ found that heating the walls of his tube with a Bunsen burner enormously increased the leak. In one instance where the pressure before heating was 0.0005 mm., heating for a few minutes increased the leak from  $2.2 \times 10^{-13}$  amp. to  $5 \times 10^{-9}$  amp., *i. e.*, 20,000 times, while the gas from the walls only sent up the pressure to 0.001 mm. He mentioned that this did not depend on the cleanliness of the tube. Exactly the same effects were produced after the tube had been boiled several times in pure nitric acid and rinsed out many times in distilled water. When the walls were kept cool by a water-bath no such effect was noticed. This emission of carbon monoxide from the walls of a glass tube when heated, or during a discharge, probably accounts for Horton's result with the spectroscope.

As regards the mechanism at the surface of the platinum and the phosphate which produces the positive electrification nothing is known. Wilson|| points out in a paper recently published that aluminium phosphate gives no positive leak when heated on a Nernst filament, so that the platinum must play an important rôle in the ionization of the gases present. He attributes the increase in the positive leak produced by moisture to the reaction of traces of carbon in the platinum with the water-vapour giving rise to carbon monoxide and hydrogen which readily carry away the positive electricity.

The evidence seems to show that if carbon monoxide

\* Proc. Roy. Soc. A. lxxxiv. 1910.

† Phil. Mag. xx. p. 582 (1910).

‡ Proc. Camb. Phil. Soc. xvi. p. 89.

§ Phil. Trans. A. ccvii. p. 19.

|| Phil. Mag. xxi. p. 634 (1911).

forms a sufficient proportion of the gas present its molecules carry the positive current. At the pressures used in the experiments described in the present paper, where the proportion of carbon monoxide from the walls of the vessel would be exceedingly small, the positive current is carried by groups of the gas-molecules.

### *Conclusions.*

1. The positive electricity emitted by heated aluminium phosphate forms ions in the gas present identical with the ions produced by X-rays, showing that the positive particle, whatever it is, which is emitted from the salt hands over the charge to the gas-molecules on collision.

2. The mobility of the positive ion is inversely proportional to the pressure of the gas down to a certain low critical pressure approximately proportional inversely to the density of the gas, below which pressure the mobility increases very rapidly.

3. The presence of water-vapour, which has very little effect on the mobility of the positive ion in regions where the inverse-pressure law holds, has a big effect when the pressure is below that region, making the mobility less than that required by the inverse-pressure law.

4. The rapid increase in the mobility at very low pressures may be due to the cluster of molecules forming the ion breaking up into a less complex group; or it may be due to the existence of a positive unit which exists in the free state for a short time at low pressures; or both these possibilities may hold good. Calculating the mass of the ion from the formula  $k = e\lambda/mv$  gives numbers indicating that the ion consists at ordinary pressures usually of about six molecules, and in the case of hydrogen of about twelve, round the positive charge. These groups break up at low pressures, giving an increased mobility.

5. In the cases of air and carbon dioxide the measurements at the lowest possible pressures show that the positive charge is carried by something less than the molecule of the gas. This may be due to the existence of a universal positive unit, or it may be due to hydrogen which the platinum probably contained.

In conclusion, the author expresses his sincerest thanks to Professor Sir J. J. Thomson for his kind encouragement and persistent interest in the experiments.

LXXVII. *The Radioactive Properties of High Temperature Flames.* By H. CARTER, A.R.C.Sc., B.Sc., Royal College of Science, London\*.

*Object of the Experiments.*

THERE is at the present time no well-authenticated case where radioactivity is called into existence by any artificial process. All the known phenomena in this branch of science are due to the spontaneous atomic disintegration observed in the naturally active substances.

If such an atomic disintegration can, under any circumstances, be set going artificially, it seems likely that this would occur in cases where large quantities of energy are being set free in a small volume. Such cases are those of the electric arc, the spark, and the oxyhydrogen and oxyacetylene blowpipe flames.

It is practically impossible to test with any great refinement for the emission of  $\alpha$  radiation in any of these processes, on account of the enormous ionization of non-radioactive origin already present. Very searching tests can, however, be made for  $\beta$  radiation, which may be looked for at a convenient distance from the place where energy is being dissipated. Such tests form the subject of the present paper.

*General Description.*

A gold-leaf electroscope was used throughout the tests, the method of procedure, stated very generally, being to compare the rate of leak of the electroscope when under the influence of the source with the rate of leak obtained when the electroscope was shielded from the action of the source.

The cases investigated were the electric arc, the oxyhydrogen and oxyacetylene blowpipe flames, and the electric spark.

The chief difficulties encountered were, practically speaking, common to all the cases, and were: heating of the electroscope by the source, causing temperature variations throughout a test, the presence of ionized air near the electroscope, and, in the case of the spark, choice of a suitable cover for the electroscope.

The arrangement of the electroscope is shown in the diagram attached (fig. 1), and this is, to a large extent, self-explanatory.

\* Communicated by the Hon. R. J. Strutt, F.R.S.

Fig. 1.

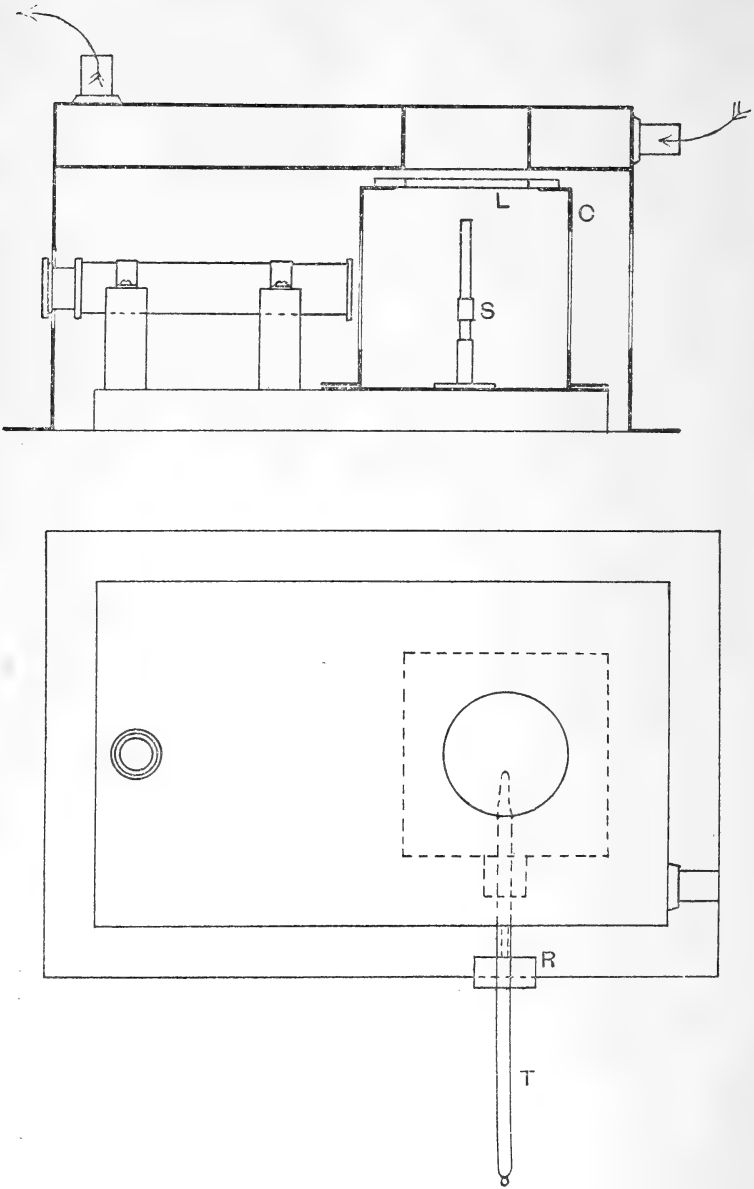
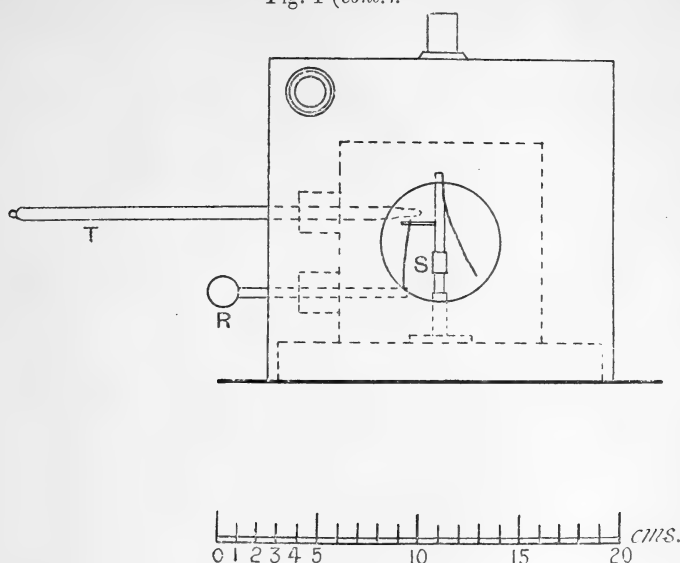


Fig. 1 (cont.).



It consisted of an electroscope in a cubical sheet zinc case C, provided with an insulated charging-rod R. The insulation of the electroscope was provided by the sealing-wax sleeve S. A thermometer T, reading up to  $30^{\circ}$  C., passed through the case and was fixed in position by paraffin-wax. The case was provided with two windows of sheet mica and a microscope with an eyepiece scale.

The cover of the electroscope, L, consisted of a diaphragm of thin metal mounted between two plates of zinc or cardboard for support. This cover and all joints in the case of the electroscope were rendered air-tight by a thick layer of paraffin-wax, thus precluding all possibility of ionized air entering the electroscope.

Temperature changes were guarded against by fitting a cover provided with a jacket for circulating water over the whole of the apparatus. This cover was painted dead black inside, so as to diminish internal reflexion and prevent photo-electric effects from disturbing the test.

The eyepiece scale was illuminated by a 16 c.p. electric lamp placed about 5 feet from the apparatus. This lamp was kept on throughout the tests, so that the illumination inside the case was always the same.

*The Direct-current Arc.*

A hand-feed arc-lamp of the type generally used for projection purposes was used. The base-plate of this lamp was screwed to the side of a small table, and in this way the arc was brought over the cover of the electroscope, and no trouble experienced with shadows from the frame and mechanism of the lamp. The distance between the arc and cover was 7 inches. A steel tube 5 feet in length and  $1\frac{1}{4}$  inch in diameter was fitted directly over the arc to assist in removing ionized air from the neighbourhood of the electroscope and to reduce the heating effect.

A sheet of copper foil 0.06 mm. thick soldered between two pieces of sheet zinc was first used as a cover, but a sheet of thin tinfoil mounted with cardboard was afterwards substituted.

The method of carrying out the test was as follows: the electroscope was charged and the circulating water turned on some time before the apparatus was required to get rid of soaking effects in the insulation of the electroscope and to allow a steady temperature to be attained. The electroscope was never allowed to become completely discharged to overcome the soaking effect. After a steady state had been reached, readings of deflexion, time, and temperature were taken at 10 minutes' interval, over periods varying from one to two hours. A thick block of iron was then placed between the cover of the electroscope and the arc, and a blank experiment run with all the other conditions precisely the same as before. By this means any light or heating effects were eliminated, so any difference found between the two rates of leak must have been due to the passage of ionizing rays through the cover of the electroscope.

As a confirmation, and in order to test the accuracy with which the rate of leak would repeat itself, variations in the method were made as follows: a blank test was run followed by an exposed test, two blank tests were run consecutively, and two exposed tests consecutively.

A large number of tests were run in this manner and curves of time and deflexion plotted in each case. Examples of these are given below (Table I. and fig. 2).



TABLE I.

Test 1.—Arc: Exposed test followed by blank test.					
Electroscope exposed.			Electroscope shielded.		
Time (minutes).	Deflexion.	Temperature (° C.).	Time (minutes).	Deflexion.	Temperature (° C.).
0	18.95	14.4	0	19.0	14.8
15	18.15	14.6	15	18.5	14.6
30	17.6	14.3	30	18.05	14.7
45	16.95	—	45	17.55	14.7
60	16.25	14.7	60	17.05	14.8
75	15.9	14.8	76	16.65	14.85
90	15.05	14.75	90	16.1	14.8
105	14.8	14.8	105	15.6	14.8
121	14.15	14.83	120	15.0	14.83
135	13.9	14.8	135	14.5	—
150	13.15	14.85			
		Mean 14.7.			Mean 14.75.

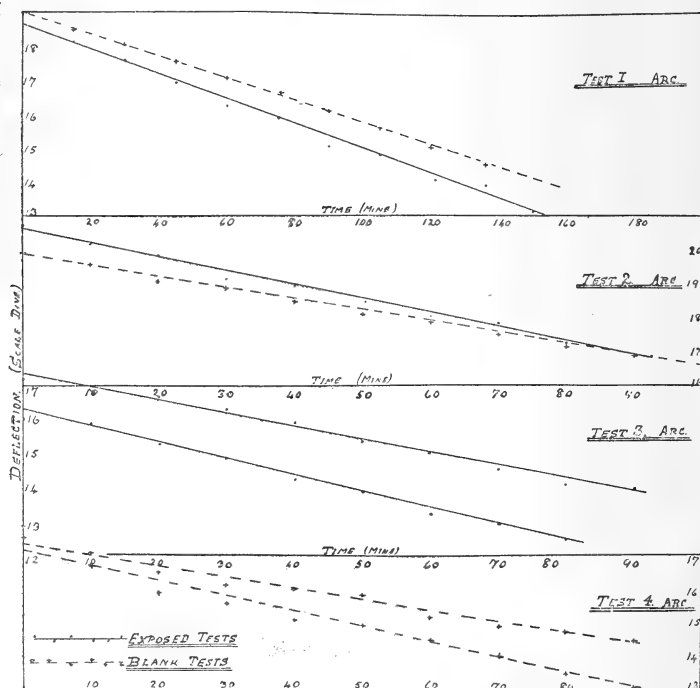
Test 2.—Arc : Shielded test followed by exposed test.					
Electroscope shielded.			Electroscope exposed.		
0	19.95	15.5	0	20.75	15.7
10	19.6	15.6	10	20.2	15.45
20	19.1	15.45	20	19.85	15.3
30	18.9	15.5	30	19.15	15.35
40	18.5	15.5	40	18.95	15.35
50	18.1	15.55	51	18.45	15.4
60	17.9	15.65	60	18.05	15.57
70	17.5	15.6	70	17.85	15.6
80	17.15	15.45	80	17.25	15.55
90	16.9	15.6	90	16.95	15.5
100	16.65	15.65			
		Mean 15.55.			Mean 15.5

Test 3.—Arc : Two consecutive exposed tests.					
0	17.2	15.93	0	16.05	16.1
10	16.95	16.03	10	15.9	16.05
20	16.8	16.2	20	15.3	16.07
30	16.35	15.9	30	14.9	16.07
40	15.95	15.7	40	14.25	16.1
50	15.4	15.9	50	13.95	16.0
60	15.05	16.05	60	13.25	16.0
70	14.55	16.1	70	12.95	15.97
80	14.1	16.1	80	12.5	15.95
90	13.95	16.03			
		Mean 16.0			Mean 16.05

TABLE I. (continued).

Test 4.—Arc: Two consecutive blank tests.					
Electroscope shielded.			Electroscope exposed.		
Time (minutes).	Deflexion.	Temperature (0° C.).	Time (minutes).	Deflexion.	Temperature (0° C.).
0	17.55	16.65	0	17.9	16.75
10	16.75	16.35	10	17.05	16.6
20	15.9	16.55	20	16.5	17.0
30	15.6	16.65	30	16.1	17.25
40	15.1	16.8	40	16.05	17.15
50	14.95	16.55	50	15.85	16.75
60	14.55	16.2	60	15.2	16.8
70	14.05	16.2	70	14.95	17.1
80	13.5	16.6	80	14.8	17.15
90	13.1	16.95	90	14.5	16.85
		Mean 16.55			Mean 16.95

Fig. 2.



*Conclusions.*

Only very small differences between the two rates of leak were obtained, and these lay within the limits within which two tests carried out under precisely the same conditions could be made to fall.

This showed that no ionizing rays capable of penetrating a thin sheet of tinfoil, after traversing the small distance in air between the arc and the cover, necessary on account of the great heating effect, were given off from the arc.

*The Oxy-Coal-gas Blowpipe.*

The general arrangement of the apparatus used in this case was exactly the same as in the previous one, except that a cowl of tin plate was fitted to the bottom of the chimney to adapt it for use with the long narrow blowpipe flame.

An ordinary injector blowpipe was used coupled to the gas-mains and an oxygen cylinder. This was held in a clamp above the outer case of the electroscope, the distance between the flame and the cover being 5 cm.

As in the last case, tests were run with blank test following an exposed one and *vice versâ*, the procedure throughout being the same.

*The Oxyacetylene Blowpipe.*

The same arrangement was again used. The same blowpipe was used and fed with acetylene from a 60 cub. ft. cylinder of dissolved acetylene supplied by the Acetylene Illuminating Co.

A non-return water-valve included was in the circuit as a safety device, but it was chiefly used as a manometer for regulating the acetylene supply. Some trouble was experienced through the popping back of the flame due to overheating of the blowpipe, but this was overcome by cooling the nozzle by means of strips of copper-foil dipping into a dish of cold water, which was frequently refilled.

The distance between the flame and the cover was again about 5 cm.

At first a good deal of trouble was experienced in getting regular readings, but this was overcome by paying special attention to the temperature regulation. The same procedure as in the previous tests was adopted.

Examples of curves and readings obtained from the two blowpipes are given below (Table II. and fig. 3).

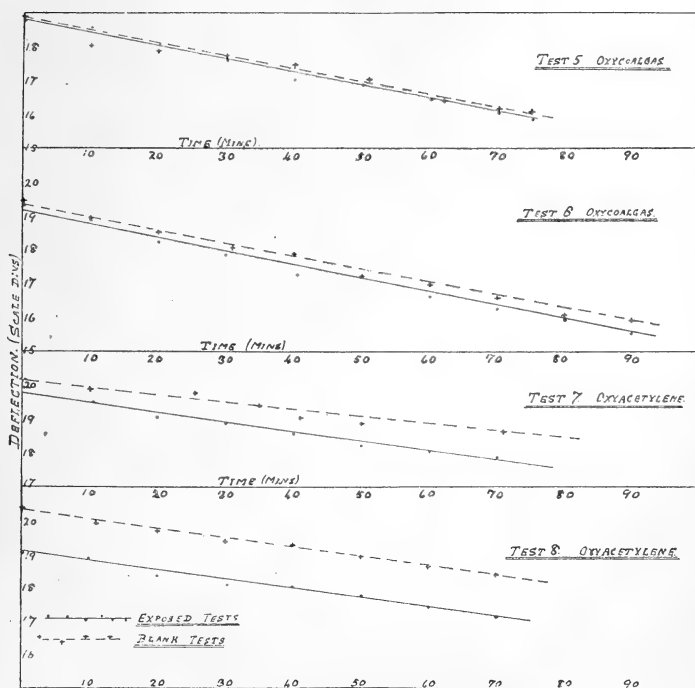
TABLE II.

Test 5.—Oxyhydrogen blowpipe : exposed test followed by blank.					
Electroscope exposed.			Electroscope shielded.		
Time (minutes).	Deflexion.	Temperature (0° C.).	Time (minutes).	Deflexion.	Temperature (0° C.).
0	18.8	13.4	0	18.9	13.1
10	18.6	13.35	10	18.15	13.2
20	18.05	13.15	20	17.9	13.55
30	17.65	13.15	30	17.85	13.55
40	17.05	13.2	40	17.5	13.25
50	16.9	13.35	52	17.05	13.15
60	16.45	13.3	64	16.4	13.4
70	16.05	13.1	70	16.2	13.55
75	15.9	13.1	75	16.1	—
		Mean 13.25			Mean 13.35
Test 6.—Oxyhydrogen blowpipe : blank test followed by exposed.					
Electroscope shielded.			Electroscope exposed.		
0	19.5	16.15	0	19.4	16.2
10	18.95	16.2	10	18.95	15.95
20	18.55	16.1	20	18.25	15.9
32	18.1	16.0	30	17.9	15.95
40	17.9	15.95	41	17.25	15.95
50	17.25	15.95	50	17.0	16.05
60	17.0	16.0	60	16.65	16.1
70	16.6	16.05	70	16.25	16.1
80	16.1	16.15	80	15.95	—
90	15.95	16.15	90	15.55	16.2
		Mean 16.05			Mean 16.05
Test 7.—Oxyacetylene blowpipe : exposed test followed by blank.					
Electroscope exposed.			Electroscope shielded.		
0	19.95	14.8	0	20.2	14.7
11	19.5	14.55	10	19.9	14.8
20	19.1	14.65	26	19.8	15.3
30	18.9	14.6	35	19.45	14.7
40	18.6	14.85	42	19.05	14.8
50	18.25	14.8	50	18.9	15.25
60	18.05	14.8	72	18.65	14.45
70	17.9	14.7			
		Mean 14.65			Mean 14.85

TABLE II. (continued).

Electroscope shielded.			Electroscope exposed.		
Time (minutes).	Deflexion.	Temperature (0° C.).	Time (minutes).	Deflexion.	Temperature (0° C.).
0	20.4	15.95	0	19.05	15.6
12	19.95	16.15	10	18.9	15.85
20	19.75	16.3	20	18.35	15.6
30	19.4	16.3	31	18.1	16.15
40	19.3	16.3	40	18.05	15.95
50	18.95	15.8	50	17.8	16.15
60	18.65	16.35	60	17.45	16.3
70	18.4	16.3	70	17.15	16.05
		Mean 16.2			Mean 16.0

Fig. 3.



*Conclusions.*

The curves obtained from the two blowpipes show practically no difference between the two rates of leak. The results are more conclusively negative than those obtained from the arc, as a much smaller distance between the flame and the cover of the electroscope could be used.

*The Electric Spark.*

For these tests a 6-inch spark-coil with hammer break run from an 18-volt supply was used. Brass rods were fitted to the ends of the ordinary sparking terminals, to bring the spark over the cover of the electroscope. A condenser was placed across the spark-gap, which was about 1 mm. in length.

The same arrangement of electroscope and water-jacket adopted in previous cases was used. In order to decrease the distance between the spark and the cover of the electroscope a small hemispherical bowl of iron fitting in the hole in the water-jacket was used as the screen in the blank experiments. The spark was kept on continuously, so that the conditions of the two tests were exactly similar.

The chief difficulty in this part of the work was found to lie in the choice of a suitable cover for the electroscope. The copper-foil used in the previous experiments and a thick tinfoil mounted with cardboard showed no difference between the rates of leak in the blank and shielded tests. A thinner tinfoil and very thin aluminium leaf mounted with cardboard were found to give way very quickly, probably on account of hot particles of brass thrown off from the electrodes and the impact of the spark. When working with these defective covers very large rates of leak were obtained in the exposed experiments, probably on account of the entrance of ionized air into the case of the electroscope, and due to the action of entladungstrahlen.

Finally, a more satisfactory cover was made by fixing a sheet of aluminium leaf to each side of a square piece of wire gauze, mounting this with cardboard, and waxing to the case of the electroscope as before.

To minimize the possibility of entrance of ionized air into the chamber of the electroscope, the steel chimney used for the other experiments was fitted, an auxiliary draught being provided by a small gas-jet burning at the end of a fine glass tube inside the chimney.

Shielded and exposed curves were now obtained as before, in which there was no appreciable difference between the two rates of leak.

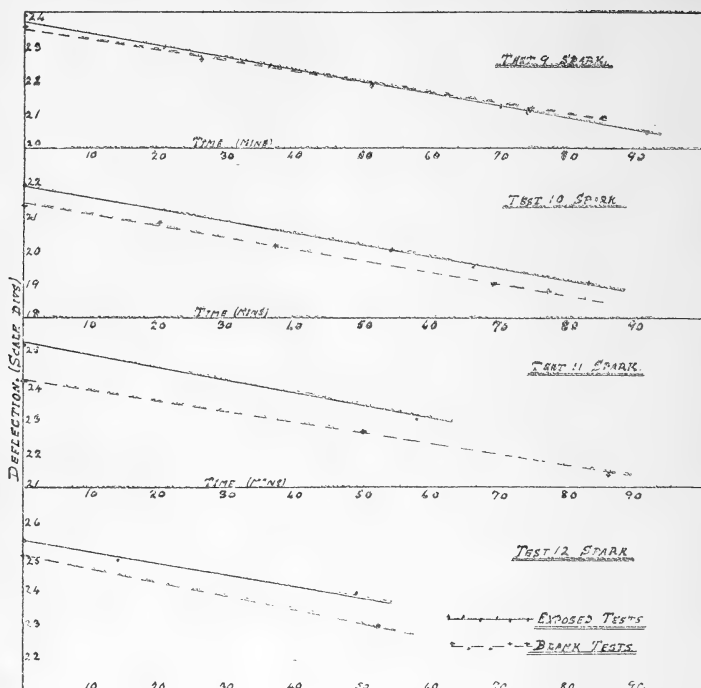
The distance between the spark-gap and the cover was 3.8 cm.

Specimens of these results are given below (Table III. and fig. 4).

TABLE III.

Test 9.—Spark : cover of copper-foil.					
Electroscope exposed.			Electroscope shielded.		
Time (minutes).	Deflexion.	Temperature (° C.).	Time (minutes).	Deflexion.	Temperature (° C.).
0	23·9	14·6	0	23·6	14·7
21	22·95	14·45	26	22·65	14·2
36	22·4	14·35	51	21·9	14·25
51	21·9	14·25	74	21·1	14·35
70	21·2	14·25	85	20·95	14·4
93	20·5	14·4			
		Mean 14·4			Mean 14·4
Test 10.—Spark : cover of thicker tinfoil.					
0	21·9	14·8	0	21·3	14·7
54	20·0	14·7	20	20·8	14·7
66	19·5	14·75	37	20·1	14·7
83	19·05	14·7	69	19·0	14·55
		Mean 14·75	77	18·8	14·5
					Mean 14·65
Test 11.—Spark : cover of aluminium leaf with wire gauze.					
Electroscope shielded.			Electroscope exposed.		
0	24·05	16·6	0	25·2	16·5
50	22·65	16·45	23	24·6	16·55
86	21·3	16·5	58	23·0	16·4
		Mean 16·5			Mean 16·5
Test 12.—Spark : cover of aluminium leaf with wire gauze.					
0	25·0	17·6	0	25·4	17·8
52	22·9	17·7	14	24·9	17·9
		Mean 17·65	49	23·9	—
					Mean 17·85

Fig. 4.



### Conclusions.

These results show that the amount of  $\beta$  radiation given off from the spark is exceedingly small, if any at all exists. It is most certainly not large enough to account for any appreciable fraction of the ionization product.

In conclusion, I wish to express my thanks to Prof. Strutt for the valuable advice he has offered throughout the work, and the continued interest he has taken in its progress.

## LXXVIII. *The Mode of Conduction in Gases.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN the reply by Sir Oliver Lodge to a letter I wrote to the Editors on the mode of conduction in gases, published in the last number of the Philosophical Magazine, it is stated, "It is plain that Professor Townsend regards with



favour, or, shall we say, holds quite dogmatically, the opinion that electric convection in a partial vacuum is effected entirely by negatively charged carriers."

This statement is incorrect, as I never held such an opinion, and no such explanation of electric convection is to be found in any of the papers I have written on that subject.

How inconsistent the above statement is with the theory of sparking which I have published, may be seen if I mention the simplest case of the application of the theory of ionization by collisions to the explanation of the sparking potential for parallel plates in a gas, at pressures above the critical pressure. All the leading features of the phenomena can be explained on the supposition that *equal numbers of positive and negative ions are generated by the collisions of the ions with the molecules of the gas*. A preliminary account of this theory was given in the 'Electrician,' April 3rd, 1903, and it was more fully described in a paper published in the Philosophical Magazine, November 1903, and in subsequent communications.

The underlying principle, which is not of dogmatic origin but is founded on experimental evidence, is as follows. When negative ions are set free from a metal plate by the action of ultra-violet light, and travel through a distance  $d$  to a parallel plate under a constant force  $X$  in a gas at constant pressure  $p$ , the number of ions  $n$  that arrive at the positive electrode is given by the formula  $n = n_0 \epsilon^{ad}$ , where  $n_0$  is the number of ions set free from the negative electrode, the remainder  $n_0(\epsilon^{ad} - 1)$  being the number generated in the gas. The quantity  $\alpha$  represents the number of positive or negative ions generated per centimetre by the collisions of a negative ion with molecules of the gas, and can easily be determined for any given force and pressure. The formula for  $n$  holds for short distances; but when  $d$  becomes large the action of the positive ions begins to have an appreciable effect on the currents. If  $\beta$  is the number of positive or negative ions produced per centimetre by a positive ion in traversing a centimetre of the gas, then the total number of negative ions arriving at the positive electrode is  $n = n_0 \frac{(\alpha - \beta) \epsilon^{(\alpha - \beta)d}}{\alpha - \beta \epsilon^{(\alpha - \beta)d}}$ , the two formulæ giving the same values of  $n$  for the shorter distances as  $\beta$  is small compared with  $\alpha$ . The effects of the positive ions may thus be obtained from the currents obtained with the larger values of  $d$  when the conductivity is maintained with potentials less than the sparking potential, by the multiplication of the ions set free by the light from the negative electrode.

The values of  $\alpha$  and  $\beta$  can thus be determined for any force  $X$  and pressure  $p$ , and it will be seen that when the distance between the plates is further increased, and the point is reached which makes the quantity  $\beta e^{(\alpha-\beta)d}$  equal to  $\alpha$ , the denominator of the above fraction vanishes, so that  $n$  becomes infinite, and a current continues to flow in the gas when the action of the light is stopped. According to the theory, therefore, the sparking potential for the distance

$d_1$  is  $X \times d_1$ ,  $d_1$  being given by the equation  $d_1 = \frac{1}{\alpha - \beta} \log \left( \frac{\alpha}{\beta} \right)$ .

When tested experimentally it has been found that the sparking potential for the distance  $d_1$  agrees accurately with the theoretical potential in the fifty or sixty cases in which the theory has been tested with various gases at different pressures. All the ions in the discharge are on this theory generated from the molecules of the gas, so that positive and negative ions in equal numbers take part in conducting the electricity. Other theories may possibly be proposed which will account equally well for the observed phenomena; at the present time I know of none that do, as the opinions or views such as those mentioned by Sir Oliver Lodge are founded on very loose arguments which break down immediately they are looked into carefully.

Sir Oliver Lodge in his recent letter maintains that there is something in his theory of the action of the "inconspicuous" positive ions, as he has found certain passages with which it is consistent in the volume of 'Recent Researches' published by Professor Sir J. J. Thomson in 1893. No doubt the further one goes back the more likely is one to find something consistent with the properties attributed to the "inconspicuous" positive ions; but even in 1889 no theory of the kind was generally accepted; and in a remarkable paper published by Giese (W. Giese, *Annalen der Physik und Chemie*, xxxvii. pp. 576-609, 1889) it was shown most definitely that explanations of the conductivity of gases founded on the theory that molecules or ions become charged by contact with electrodes were absolutely inconsistent: and it is interesting to note that it was on the principles formulated by Giese to explain the phenomena of the conductivity of flames that much of the modern advance in the theory of the Conductivity of Gases has been made.

JOHN S. TOWNSEND.

Electrical Laboratory, Oxford.  
7th October, 1911.

LXXIX. *Notices respecting New Books.*

*Gesammelte Abhandlungen von* FRIEDRICH KOHLRAUSCH. Edited by WILHELM HALLWACHS, ADOLF HEYDWEILLER, KARL STRECKER, and OTTO WIENER. First volume. With a portrait of the Author. Pp. xxxv+1108. (Leipzig: J. A. Barth, 1910.)

THIS collected edition of the scientific papers of the late Dr. Kohlrausch represents his life-work. His last manuscript was finished scarcely two weeks before his death in January 1910, and during the previous Christmas-time he had been planning fresh work in collaboration with Dr. Grüneisen. No more fitting monument then could be erected to him than that formed by bringing together his various contributions to science. The present volume includes only the first portion of his numerous investigations, viz. those dealing with Electricity, Heat, Optics, absolute electrical measurements, and miscellaneous topics. The second volume will contain his papers on Electrolysis. In each of the above subjects the separate papers are in general arranged in the order of their first appearance; a list of the papers in this order serves as a general index. A second list is included, giving all his papers in order of appearance. The number of each page of the journal, in which any part originally appeared, is given by a number inserted in square brackets in the text; so that a reference to the original can be quoted from this collection itself.

A glance through this collection is sufficient to remind one of the important part which Kohlrausch has played toward making physics into an exact science. Probably the most noteworthy of his contributions under this head are those on the electrochemical equivalent of silver (pp. 668-726) and on the absolute value of the electrical conductivity of mercury (pp. 763-885). Both of these investigations reveal the nature of the man. Of work of a less precise nature we may cite his investigations on "elastische Nachwirkung," occupying practically the whole of the first 162 pages of this volume and including his earliest published work. These are only particular instances; his varied activities will be better gauged from the statement that 113 separate productions are quoted in this volume alone. Every physical investigator will be glad to have them in their collected form.

*Outlines of the Theory of Electromagnetism.* By GILBERT T. WALKER, M.A., Sc.D., F.R.S. Pp. 52. Cambridge University Press, 1910. 3s. nett.

THIS small book consists of a summary of a series of lectures delivered before the Calcutta University. It does not claim to any originality except in the mode of presenting the subject. It forms a most convenient outline of the subject on vectorial lines. The first chapter is as useful an introduction to vector analysis as

we have seen. The author is very clear in the way in which he demonstrates the insufficiency of the Maxwell-Hertz equations for moving media, and outlines the electronic theory of Lorentz. Perhaps it is mainly a question of taste, but we do not like the use of the term *polarisation* instead of *induction*. We are in the habit of regarding the term  $4\pi I$  as standing for polarisation.

# LXXX. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

April 26th, 1911.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

[Continued from p. 468.]

Dr. J. D. FALCONER, M.A., F.G.S., gave an account of the Geology of Northern Nigeria, illustrating his remarks by means of lantern-slides. He pointed out that the Protectorate of Northern Nigeria covers an area of about 255,000 square miles, over half of which crystalline rocks are exposed at the surface. A series of hard banded gneisses of an Archæan type is intermingled with a series of quartzites, phyllites, schists, and gneisses of sedimentary origin, in such a way as to suggest that the two series, while originally unconformable, have been at a later period affected by a common folding and foliation along axes which are predominantly meridional in direction. The two series have also been pierced by numerous igneous intrusions of a granitic type, which are subdivided into (1) an older, wholly or partly foliated group, and (2) a younger non-foliated group, characterized by the predominance of soda-bearing types.

Folded and faulted rocks of Cretaceous age are found in the valleys of the Benue and the Gongola. They consist of a lower series of sandstones and grits, in places salt-bearing, and an upper series of limestones and shales with numerous fossils of Turonian age. These Cretaceous rocks are overlain unconformably by a horizontal series of sandstones, grits, conglomerates, and ironstones, which in Sokoto province contains intercalations of Middle Eocene limestone. Considerable volcanic activity occurred during Tertiary times, and gave rise to extensive fields of basaltic lava in Bauchi and Bornu, as also to numerous puyes of trachyte, phonolite, olivine-basalt, and nepheline-basalt throughout Southern Bauchi, Muri, and Yola. Repeated minor oscillations of the crust occurred during the latter part of the Tertiary Era, and culminated in the elevation of the Bauchi plateau, the depression of the Chad area, and the establishment of the present river-system.

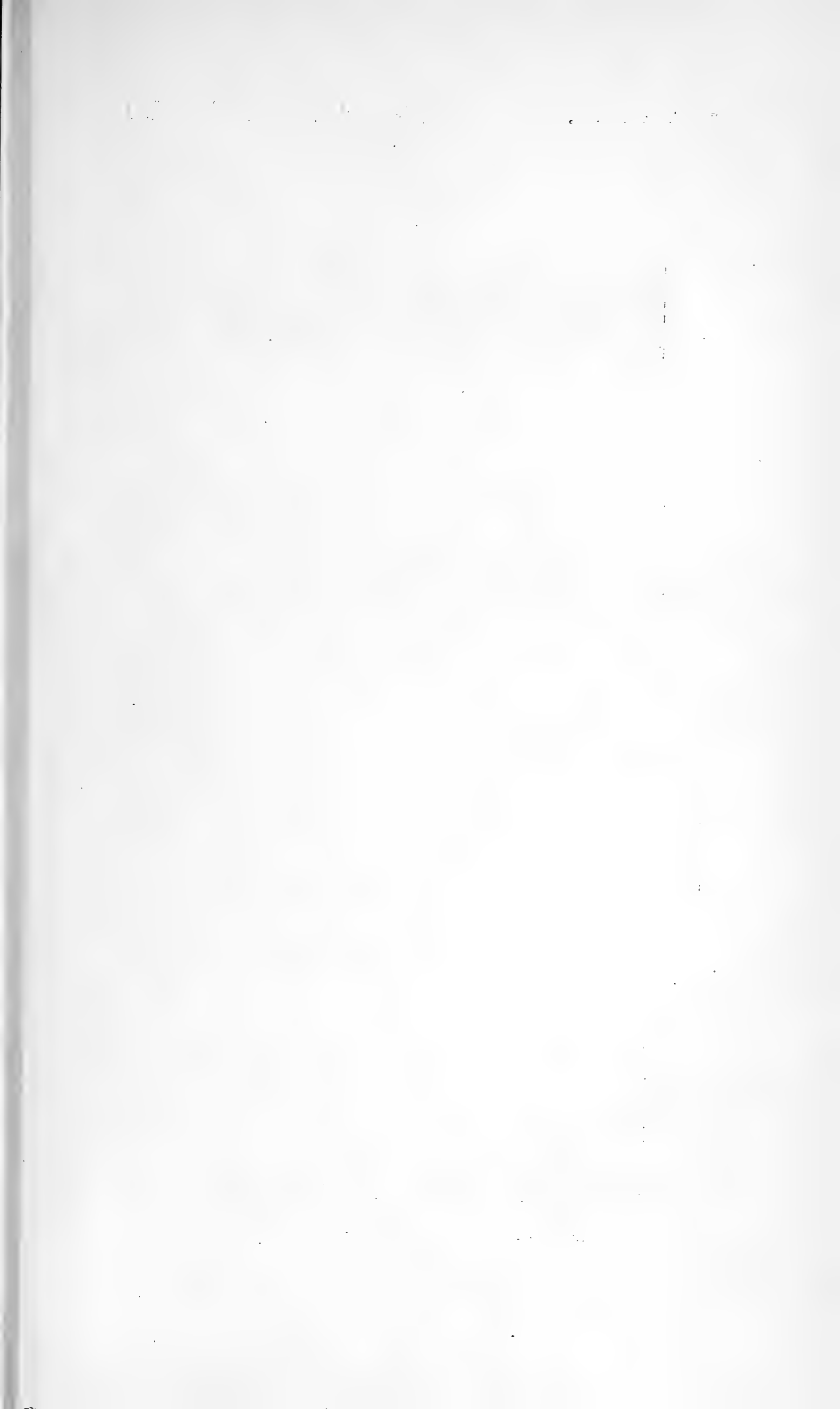
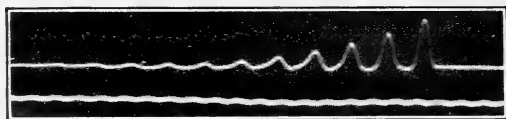


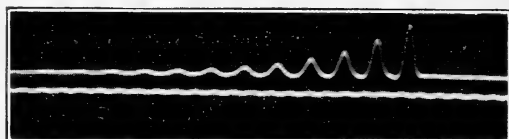
FIG. 8.



Case I.

$i_0 = 5.05$  amperes.

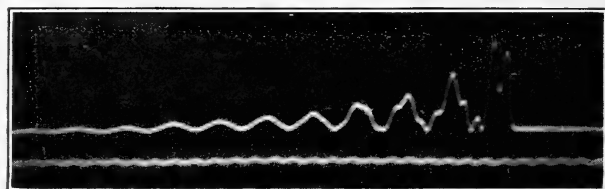
FIG. 9.



Case II.

$i_0 = 4.02$  amperes.

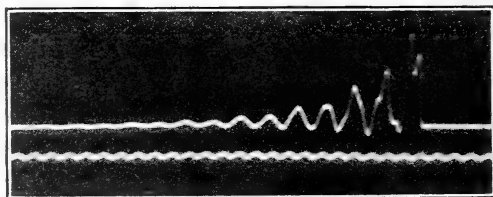
FIG. 10.



Case III.

$i_0 = 9.1$  amperes.

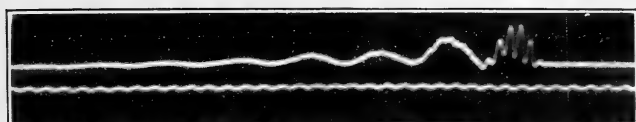
FIG. 11.



Case IV.

$i_0 = 5.8$  amperes.

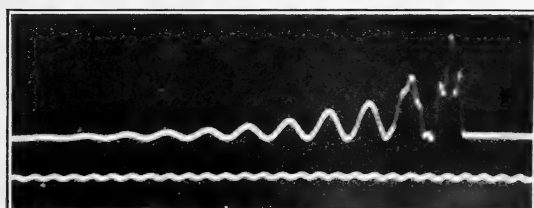
FIG. 12.



Case V.

$i_0 = 4.3$  amperes.

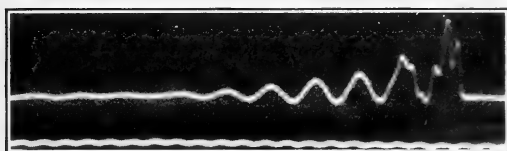
FIG. 13.



Case VI.

$i_0 = 4.44$  amperes.

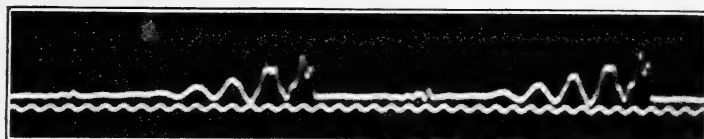
FIG. 14.



Case VII.

$i_0 = 2.4$  amperes.

FIG. 15.



Case VII with motor interrupter.

THE JOURNAL OF THE

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1911





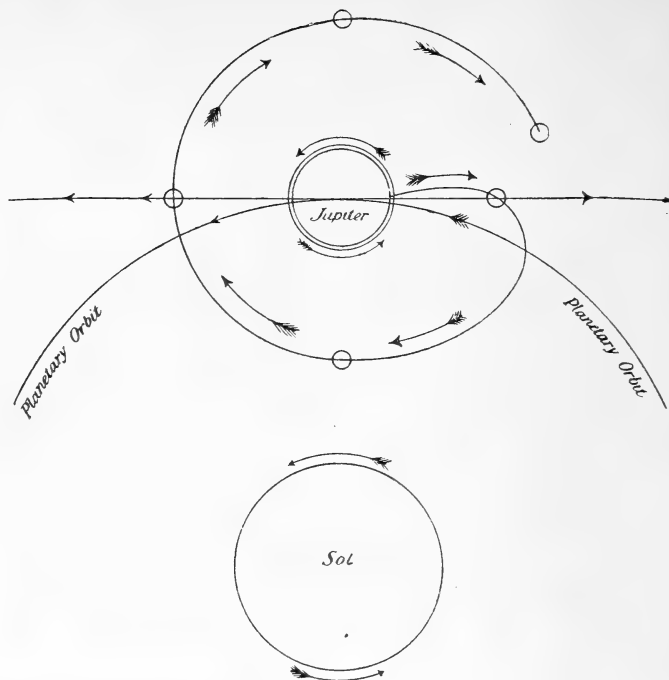


FIG. 1.—COMETARY SATELLITES WITH RETROGRADE MOTION.

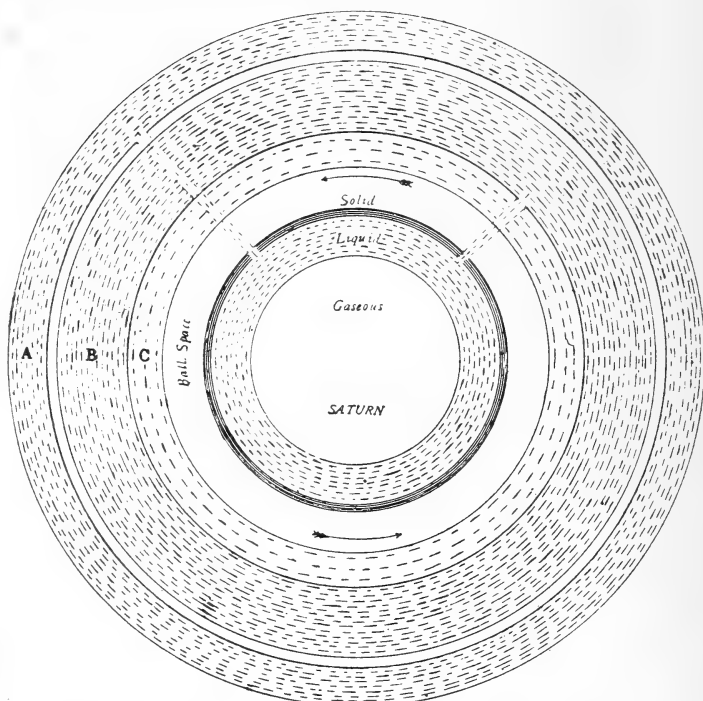
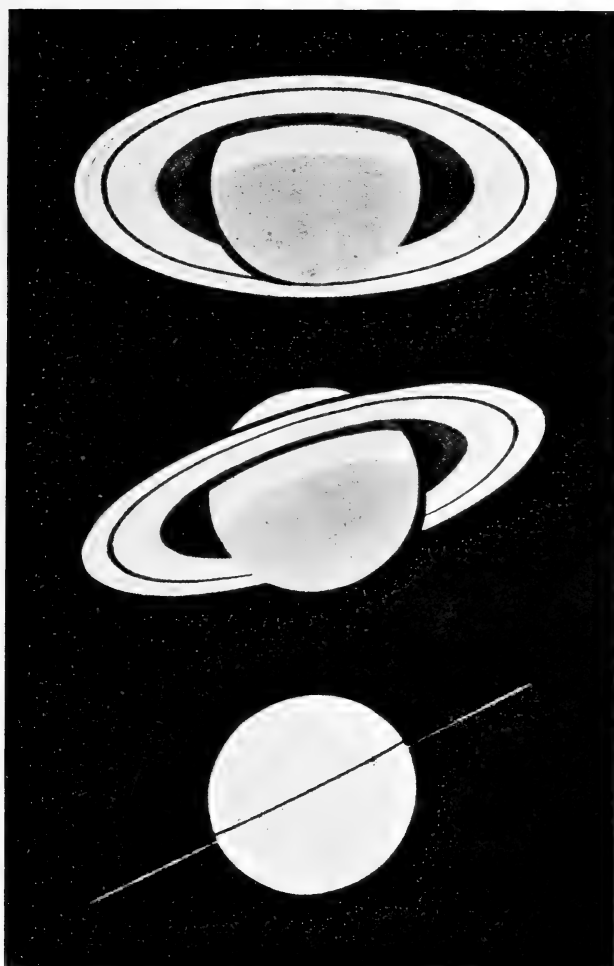


FIG. 2.—SCALED DIAGRAM OF SATURN'S RINGS.





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LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[SIXTH SERIES.]

D E C E M B E R 1911.

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LXXXI. *On the Amount of the Radioactive Products present in the Atmosphere.* By S. KINOSHITA, S. NISHIKAWA, and S. ONO\*.

*Introduction.*

(1) **I**T is well known that in 1901 Ester and Geitel† collected radioactive matter from the atmosphere on a negatively charged wire, in exactly the same way as Rutherford‡ had done for thorium deposit. This active matter was shown later by Bumstead§ to consist of the active deposits of both radium and thorium, which originated in the corresponding emanations present in the atmosphere. A number of experiments on this subject have since been made at various parts of the earth's surface, the dependence of the amount of deposits on the meteorological conditions being chiefly investigated. Although this method is supposed not to be suited for determining the amount of the emanation itself, it is the only way of estimating the relative amounts of the radium and thorium emanations in the atmosphere. This has been done by Dadourian|| and W. Wilson¶, to whose work references will be made later.

\* Communicated by Prof. E. Rutherford, F.R.S., having been read on the 3rd June at the Tokyo Mathematico-Physical Society.

† Elster and Geitel, *Phys. Zeit.* ii. p. 590 (1901).

‡ Rutherford, *Phil. Mag.* Jan. and Feb. 1900.

§ Bumstead, *Amer. Journ. Sci.* vol. xviii. p. 1 (1904).

|| Dadourian, *Le Radium*, April 1908.

¶ W. Wilson, *Phil. Mag.* Feb. 1909.

*Phil. Mag.* S. 6. Vol. 22. No. 132. Dec. 1911.

3 I

pg 821

Our principal object in the present experiments was to find the relative amounts of these two emanations at Tokyo. We have then attempted to elucidate the procedure of deposition of the active matters on a negatively charged wire.

When this paper was ready to appear, *Traité de Radioactivité*, by Madame Curie, came in our hand, in which similar problems are dealt with\*. We have, however, treated the problem from a different point of view, of which the full account will be here given.

### *Experiments.*

(2) Two copper wires, each .5 mm. thick, 27 metres long, and insulated at both ends, were horizontally stretched in the N.S.-direction between two posts at the heights of 6.5 and 1.5 metres respectively from the ground in the south yard of our laboratory building. These wires were connected to the negative terminal of a Wimshurst machine driven by a motor and maintained at a potential of about -11,000 volts, which was measured with a Kelvin electrostatic voltmeter.

When the wires had been exposed to the atmosphere for a definite time (usually 4 hours, in some cases 24 hours), they were removed, and the middle portion, 20 metres long, of each was quickly coiled round a brass cage 9.2 cm. square, which was then introduced into a square electroscope with sides 11.3 cm. The activity of the deposits on each wire was then measured in the usual way for about a day. We expressed it in terms of the scale divisions on an ocular micrometer divided in  $\frac{1}{10}$  mm. passed by the gold-leaf per second. As a matter of fact, the rates of discharge of the two electroscopes were not exactly the same. We have, therefore, reduced them to a common standard by the aid of the  $\gamma$ -rays from a radium preparation placed at equal distances from the electroscopes, when the wires were not active. The four rods constituting the side-frames of the cages were provided each with 55 grooves in regular intervals of  $\frac{1}{6}$  cm., which served to keep a wire in the same definite position.

The decay-curve of the activity thus obtained can be satisfactorily explained by the assumption, as has hitherto been made, that radium A and thorium A were deposited on the wire during exposure.

Although we were not able to measure accurately the activity of the radium A, on account of its rapid decay—a few minutes being unavoidably lost in winding the wires in electroscopes—the activity due to radium C and also to the thorium deposits, and consequently their corresponding values

\* *Traité de Radioactivité*, vol. ii. p. 484 (1910).

for an infinitely long exposure, could be easily deduced with fair accuracy from the decay-curves.

The experiments were commenced in April and finished in December 1910\*. Some of the results are given in Table I. (p. 824). The meteorological data in the table are taken from 'Monthly Report of the Central Meteorological Observatory of Japan.' The observatory is situated about two miles south of our laboratory.

In this series of experiments the time of exposure was 4 hours, *i. e.* from 9 A.M. to 1 P.M., except in the second observation on the 19th, in which it was from 2 to 6 P.M., and the corresponding values in Column X. must be understood as those at 3 and 5 P.M.

(3) The Table shows that, in this series of experiments :—

(a) the activities due to the radium C in equilibrium were 3.14 and 3.33 respectively for the upper and lower wires, on the average (it may be added that the average values in all the series of our experiments were 4.06 and 4.28 respectively for the upper and lower wires) ;

(b) their extreme values were as 3 : 1 (those in all the series of the experiments were as 9 : 1) ;

(c) the ratio of the amount of the radium C on the upper and lower wires was nearly constant and equal to .95, on the average ;

(d) the activities due to the thorium deposits were 1.34 and 2.62 respectively for the upper and lower wires, on the average (those in all the series of the experiments were 1.08 and 2.20 respectively) ;

(e) the relative amounts of the thorium deposits on the upper and lower wires were by no means constant, but varied over a wide range on different occasions, and therefore

(f) the relative amounts of the radium and thorium deposits were not constant, but depended on the height at which the wire had been exposed.

#### *Theoretical Considerations.*

(4) Considering the comparatively slow rate of transformation of the radium emanation, and the existence of some convection current of air even on calm days, it will be reasonable to suppose that the amount of the emanation does not appreciably vary within a few metres above the earth's surface. Let  $N_E$  denote the number of atoms of the emanation in each c.c. of air. These uniformly distributed atoms of the

\* One of us (S. Ono) having left the Laboratory in July 1910, we were assisted in the later part of the experiment by Mr. T. Sone, to whom our thanks are due.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.		XI.	XII.	XIII.	XIV.	XV.
Date.	Radium C.		ThB+ThC.		ThB+ThC.		Radium C ThB+ThC		Direction and velocity of wind at		Mean barome- tric height during exposure.	Rel. humidity during exp.	Mean tempera- ture during exposure.	Rainfall.	Duration of sunshine during exp.
	Upper wire.	Lower wire.	Upper wire.	Lower wire.	Upper wire.	Lower wire.	Upper wire.	Lower wire.	10 A.M.	Noon.					
May 16 ...	2.30	2.27	1.01	.30	1.23	.24	7.67	1.85	NW	1.5 NW	757.1	80	17.5	7.2	0
" 17 ...	2.83	2.92	.97	.65	1.16	.56	4.35	2.52	NE	2.8 SE	760.0	66	17.4	0	28
" 18 ...	1.97	2.00	.98	.96	1.69	.57	2.05	1.18	ESE	3.0 SE	758.1	63	18.9	0	31
" 19 ...	5.81	6.45	.90	1.70	2.55	.67	3.42	2.86	NNW	5.6 NNW	752.0	46	18.4	0	37
" 19 ...	5.60	5.79	.97	2.60	3.62	.72	2.15	1.60	NW	10.1 NW	751.0	32	19.4	0	40
" 20 ...	3.74	3.98	.94	2.26	3.65	.62	1.65	1.09	NW	6.1 NNW	753.1	40	18.4	0	34
" 21 ...	2.21	2.41	.92	1.16	3.71	.31	1.89	.65	NNW	2.0 W	764.1	69	17.1	.3	0
" 22 ...	...	...	...	...	...	...	...	...	NNW	2.2 N	759.8	65	18.1	.1	.6
" 23 ..	2.84	2.57	.91	1.19	3.10	.38	1.97	.83	NE	1.6 SE	758.8	54	21.0	0	40
" 24 ...	2.10	2.25	.93	1.13	2.56	.44	1.86	.89	NNW	1.3 SSE	760.8	60	21.3	0	40
" 25 ...	2.47	2.65	.93	1.42	2.94	.48	1.75	.90	N	2.0 SE	761.1	54	22.3	0	40
Average ...	3.14	3.33	.95	1.34	2.62	.50	2.88	1.44							



emanation produce atoms of radium A *in situ*, and these in turn quickly change into atoms of radium B, and so on. Consequently, the distribution of the atoms of radium A must be very nearly uniform, and their number in each c.c. will be  $\frac{\lambda_E N_E}{\lambda_A}$ , if  $\lambda_E$  and  $\lambda_A$  are the constants of transformation of the emanation and of radium A respectively.

(5) Rutherford\* has shown that the carriers of the active deposits of radium and thorium move through a gas under an electric field with a velocity  $v$  which is proportional to the intensity  $F$  at that point, thus

$$v = kF.$$

It was found that  $k$  is nearly the same for the carriers of both radium and thorium deposits, and equal to about 1.3 cm. per second for a potential gradient of 1 volt per cm. in air at standard pressure and temperature.

These particles, in addition to the action of the electric field, may be conveyed by a current of air.

(6) Starting from the above assumptions, we shall find the number of the particles of radium A deposited on unit length of a wire in unit of time, when it is stretched at a height of  $h$  above the ground, and raised to a negative potential  $-V$ .

For convenience of calculation, it is assumed that the wire is infinitely extended with the charge  $-\mu$  per unit length.

We shall first consider the case in which a wind of velocity  $w$  is blowing horizontally in the direction of  $x$ , perpendicular to the length of the wire. Take the axis  $OX$  on the section of the surface of the earth by a plane perpendicular to the length of the wire, and  $OZ$  on the vertical line passing through A, the position of the wire. Let  $A'$  be the image of A with respect to  $OX$ , so that

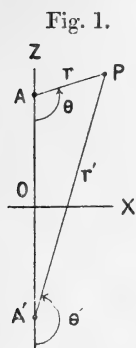
$$OA = OA' = h.$$

The component-velocities of a particle at point  $P(x, z)$  are given by

$$\frac{dx}{dt} = 2\mu k \left( \frac{x}{r'^2} - \frac{x}{r^2} \right) + w,$$

$$\frac{dz}{dt} = 2\mu k \left( \frac{z+h}{r'^2} - \frac{z-h}{r^2} \right),$$

\* Rutherford, Phil. Mag. vol. v. p. 103 (1903). See also Franck, *Verh. d. D. Phys. Ges.* Oct. 1909.



where  $r$  and  $r'$  are the distances of  $P$  from  $A$  and  $A'$  respectively.

It will be seen that the motion is analogous to an irrotational motion of liquid in two dimensions, and there exists a velocity-potential

$$\phi = -2\mu k \log \frac{r'}{r} - wz,$$

which satisfies the equations

$$-\frac{\partial \phi}{\partial x} = \frac{dv}{dt} \quad \text{and} \quad -\frac{\partial \phi}{\partial z} = \frac{dz}{dt}.$$

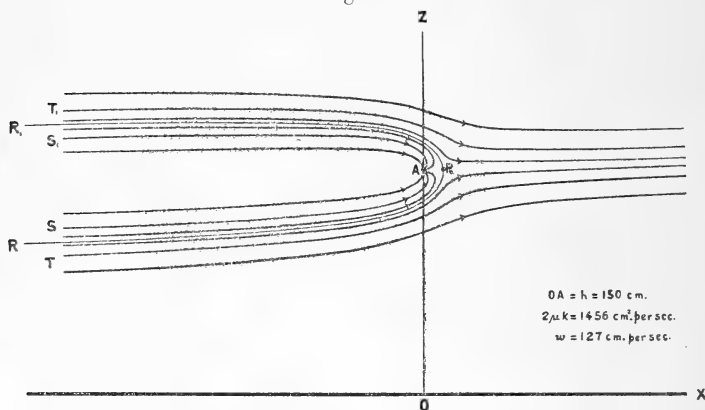
The stream-function  $\psi$ , which is orthogonal to the function  $\phi$ , can be represented by

$$\psi = -2\mu k (\theta' - \theta) - wz,$$

where  $\theta$  and  $\theta'$  denote the angles which  $r$  and  $r'$  make respectively with the axis of  $z$ .

To show the path of the particles, we have, in fig. 2,

Fig. 2.



graphically traced the curve  $\psi = \text{const.}$ , or

$$2\mu k (\theta' - \theta) + wz = c,$$

where  $c$  is a parameter.

Let  $x_0, z_0$  be the coordinates of a point at which the particle has no velocity, *i. e.*, the velocity of the particle due to the electric field is equal and opposite to that due to the wind.

They are found by solving the equations

$$\frac{\partial \phi}{\partial x} = 0 \quad \text{and} \quad \frac{\partial \phi}{\partial z} = 0.$$

Remembering that  $r^2 = x^2 + (z-h)^2$  and  $r'^2 = x^2 + (z+h)^2$ , and writing  $p$  for  $\frac{4\mu k}{wh}$ , we get

$$x_0^2 = \frac{h^2}{2}(\sqrt{1+p^2}-1), \text{ and } z_0^2 = \frac{h^2}{2}(\sqrt{1+p^2}+1).$$

If  $r_0, r'_0, \theta_0$ , and  $\theta'_0$  are the values of  $r, r', \theta$ , and  $\theta'$  respectively for  $x=x_0$  and  $z=z_0$ , then

$$\cos(\theta'_0 - \theta_0) = \frac{r_0^2 + r_0'^2 - 4h^2}{2r_0 r_0'} = \frac{\sqrt{1+p^2}-1}{p}.$$

Therefore a branch of the curve which passes through  $x_0, z_0$  is given by the equation

$$\theta' - \theta - \cos^{-1} \frac{\sqrt{1+p^2}-1}{p} + \frac{2}{p} \left( \frac{z}{h} - \sqrt{\frac{\sqrt{1+p^2}+1}{2}} \right) = 0,$$

and graphically represented by  $RP_0$ . It will be seen that the other branch  $R_1P_0$  can be represented by

$$\theta' - \theta - \left( \cos^{-1} \frac{\sqrt{1+p^2}-1}{p} + 2\pi \right) + \frac{2}{p} \left( \frac{z}{h} - \sqrt{\frac{\sqrt{1+p^2}+1}{2}} \right) = 0.$$

These curves divide the space into two regions. All the particles within the region  $RP_0R_1$ , such as at  $S$  or  $S_1$ , reach the point  $A$ , *i. e.* they are caught by the wire, while those outside the region, such as at  $T$  or  $T_1$ , escape from it. We shall call the region within the surface  $RP_0R_1$ , the "*effective region*."

(7) Since  $\lambda_E N_E$  is the number of particles of radium  $A$  produced per second per c.c. of air, that produced in an elementary volume  $ds_1 ds_2 dl$  at  $P$  will be

$$\lambda_E N_E ds_1 ds_2 dl \text{ per second,}$$

where  $ds_1$  and  $ds_2$  denote the line-elements of the curves  $\phi = \text{const.}$  and  $\psi = \text{const.}$  respectively, and  $l$  denotes the distance measured in the direction of the wire.

After an interval of time  $t$ , which is taken by these particles to reach the wire, the number will be decreased to

$$\lambda_E N_E e^{-\lambda_A t} ds_1 ds_2 dl,$$

provided that the recombination of the particles with the negative ions present in the air be disregarded.

Since the velocity of the particle  $f$ , say, is equal to  $-\frac{\partial\phi}{\partial s_2}$  or  $-\frac{\partial\psi}{\partial s_1}$ , we get

$$t = \int \frac{ds_2}{\text{velocity}} = \int \frac{ds_2}{-\frac{\partial\phi}{\partial s_2}} = - \int_{\phi}^{-\infty} \frac{d\phi}{f^2} = \int_{-\infty}^{\phi} \frac{d\phi}{f^2},$$

as we may put  $\phi = -\infty$  at A for the calculation of  $t$ .

Therefore the number  $Q$  of the particles deposited on unit length of the wire in unit of time is

$$\begin{aligned} Q &= \lambda_E N_E \iint e^{-\lambda_A t} ds_1 ds_2 = \lambda_E N_E \int_{\psi_1}^{\psi_2} \int_{-\infty}^{\phi_1} e^{-\lambda_A \int_{-\infty}^{\phi} \frac{d\phi}{f^2}} d\phi d\psi \\ &= \frac{\lambda_E N_E}{\lambda_A} \int_{\psi_1}^{\psi_2} \left\{ 1 - e^{-\lambda_A \int_{-\infty}^{\phi_1} \frac{d\phi}{f^2}} \right\} d\psi. \quad \dots (A) \end{aligned}$$

The limits of integration  $\psi_1$ ,  $\psi_2$ , and  $\phi_1$ , which are functions of  $\mu k$ ,  $h$ , and  $w$ , must be so taken that the integration extends over the whole effective region  $RP_0R_1$ .

If this boundary curve  $RP_0R_1$  does not cut the axis of  $x$  at a finite distance, then

$$\phi_1 = \infty, \quad e^{-\lambda_A \int_{-\infty}^{\infty} \frac{d\phi}{f^2}} = 0.$$

Therefore

$$Q = \frac{\lambda_E N_E}{\lambda_A} \int_{\psi_1}^{\psi_2} d\psi = 4\pi\mu k \frac{\lambda_E N_E}{\lambda_A}. \quad \dots (B)$$

It must be noticed that the above expression is independent of  $w$ . If the boundary curve  $RP_0R_1$  does cut the axis of  $x$  at a finite distance, then  $Q$  will be less than the value above obtained.

(8) We shall now find the condition that  $RP_0$  does not cut the axis of  $x$  at a finite distance. The condition will be satisfied if  $\theta' - \theta = 2\pi$  for values of  $z$  such that  $0 < z < h$ , i. e., if

$$2\pi \leq \cos^{-1} \frac{\sqrt{1+p^2}-1}{p} + \frac{2}{p} \sqrt{\frac{\sqrt{1+p^2}+1}{2}}$$

$$\text{or } p \leq .415 \quad \text{or } w \geq \frac{4\mu k}{.415 \times h}.$$

Consequently, if  $w \geq \frac{4\mu k}{.415 \times h}$  cm. per second, then the boundary of the effective region tends to become parallel to

OX. From the values of  $h$ ,  $k$ , and  $\mu$  which will be given later on, it is found that

$$\frac{4\mu k}{\cdot 415 \times h} = 10.8 \text{ cm. per sec. for } h = 650 \text{ cm., and}$$

$$\frac{4\mu k}{\cdot 415 \times h} = 40.0 \text{ cm. per sec. for } h = 150 \text{ cm.,}$$

when the wires are charged at  $-11,000$  volts. It will be seen that a slight wind is sufficient to satisfy that condition.

(9) As a special case, if  $w=0$ ,  $\phi=\text{const.}$  represents a system of circles which have their centres on the axis of  $z$ , and  $\psi=\text{const.}$  another system of circles which pass through A and have their centres on the  $x$ -axis. In this case the limits of integration with respect to  $\phi$  are to be taken from  $-\infty$  to 0, the value of  $\phi$  at the surface of the earth, where the stream-lines end. Thus

$$Q = \frac{\lambda_E N_E}{\lambda_A} \int_{\psi_1}^{\psi_2} \left\{ 1 - e^{-\lambda_A \int_{-\infty}^0 \frac{d\phi}{f^2}} \right\} d\psi.$$

Now, since  $ds_1 = \sec \theta dr' = \sec \theta' dr$ ,

$$d\phi = -2\mu k \left( \frac{dr'}{r'} - \frac{dr}{r} \right) = -\frac{4\mu k h}{rr'} ds_1,$$

$$\therefore ds_1 = -\frac{rr'}{4\mu k h} d\phi.$$

Similarly,  $ds_2 = -\frac{rr'}{4\mu k h} d\psi$ ,

$$\therefore f^2 = \frac{16\mu^2 k^2 h^2}{r^2 r'^2},$$

$$\int_{-\infty}^0 \frac{d\phi}{f^2} = \int_{-\infty}^0 \frac{r^2 r'^2}{16\mu^2 k^2 h^2} d\phi = \frac{h^2}{2\mu k \sin^2 \chi} (1 - \chi \cot \chi),$$

where  $\chi = \pi - (\theta' - \theta) = \pi + \frac{\psi}{2\mu k}$ .

Therefore

$$Q = \frac{2\mu k \lambda_E N_E}{\lambda_A} \int_{-\pi}^{\pi} \left\{ 1 - e^{-\lambda_A \frac{h^2}{2\mu k \sin^2 \chi} (1 - \chi \cot \chi)} \right\} d\chi.$$

It may be noticed that the second term under the integral sign diminishes rapidly as  $h$  increases.

On evaluation it was found that

$$Q = .25 \times 4\pi\mu_2k \frac{\lambda_E N_E}{\lambda_A} \quad \text{for } h=h_2=150 \text{ cm., and}$$

$$Q = .75 \times 4\pi\mu_1k \frac{\lambda_E N_E}{\lambda_A} \quad \text{for } h=h_1=650 \text{ cm.}$$

(10) When the wind is in any other horizontal direction we can consider separately the effects of two component velocities  $w_s$  and  $w_p$  perpendicular and parallel to the direction of the wire respectively, the latter of which, however, will have no effect on the value of  $Q$ , the case being the same as that in which there is no wind. We may, therefore, conclude that *the number of the particles of radium A deposited per second on each centimetre of the wire is*

$$\text{if } w_s \neq \frac{4\mu k}{.415 \times h}, \quad Q = 4\pi\mu k \cdot \frac{\lambda_E N_E}{\lambda_A}, \text{ and}$$

$$\text{if } 0 < w_s < \frac{4\mu k}{.415 \times h}, \quad .25 \times 4\pi\mu k \cdot \frac{\lambda_E N_E}{\lambda_A} < Q < 4\pi\mu k \cdot \frac{\lambda_E N_E}{\lambda_A},$$

for  $h=150$  cm.,

and

$$.75 \times 4\pi\mu k \cdot \frac{\lambda_E N_E}{\lambda_A} < Q < 4\pi\mu k \cdot \frac{\lambda_E N_E}{\lambda_A},$$

for  $h=650$  cm.

(11) The result can be obtained from another consideration. From the equations already obtained for the boundary curves  $RP_0$  and  $R_1P_0$ , it is easily seen that the depth of the effective region is  $\frac{4\pi\mu k}{w_s}$  at  $x = -\infty$ , for which  $\theta' - \theta = 2\pi$ , provided that the curve  $RP_0R_1$  does not cut the axis of  $x$  at a finite distance. Since the velocity of the particles at  $x = -\infty$  is  $w_s$  and in the direction of the  $x$ -axis,

$$\frac{4\pi\mu k}{w_s} \cdot w_s = 4\pi\mu k$$

is the quantity of air which crosses the section of the effective region of unit width at  $x = -\infty$  in the direction of  $x$  in each sec., or, in other words, the quantity of air contributing to the deposit on each cm. of the wire per second. Since  $\frac{\lambda_E N_E}{\lambda_A}$  is the number of atoms of radium A in each cubic centimetre

of the air in equilibrium,

$$4\pi\mu k \frac{\lambda_E N_E}{\lambda_A}$$

is the number of particles of radium A deposited on the wire per cm. per second, or that of radium A or radium C breaking up per second on each cm. of the wire in equilibrium, provided that there has been no recombination between the particles and the negative ions present in air. We have thus come to the same result as had already been arrived at in Art. 7, equation (B).

(12) In the actual case some of the particles do not reach the wire, as they are neutralized on their way to it by uniting with the negative ions present in air.

It will not be convenient to solve equation (A) by introducing the correction due to the recombination. Firstly, the production of ions is not uniform. It is extremely intense near the wire on which the active deposits are already collected. Secondly, the negative ions are, as soon as they are produced, set in motion, the path of which is represented by the equation

$$-2\mu k(\theta' - \theta) + wz = \text{const.}$$

The problem is complicated since the recombination takes place while the particles of radium A and the negative ions are both in motion.

An approximate solution can, however, be obtained from the consideration described in Art. 11. Let  $N_{A,+}$  be the number of the particles of radium A per cubic centimetre of the atmosphere in equilibrium when there is no electric field. Then, on the assumption that they can be treated as ordinary gaseous ions, we have

$$\frac{dN_{A,+}}{dt} = \lambda_E N_E - \lambda_A N_{A,+} - \alpha n N_{A,+} = 0,$$

where  $\alpha$  is the coefficient of recombination, and  $n$  the number of the negative ions present in each cubic centimetre of air.

If  $q$  is the rate at which the negative ions are produced,  $n = \sqrt{\frac{q}{\alpha}}$ . Therefore,

$$N_{A,+} = \frac{\lambda_E N_E}{\lambda_A + \alpha n} = \frac{\lambda_E N_E}{\lambda_A + \sqrt{\alpha \cdot q}}.$$

According to the investigations of Rutherford and others\*,

\* Rutherford and Cooke, Amer. Phys. Soc. Dec. 1902. McLennan, Phys. Rev. iv. (1903). McClelland, Phil. Mag. July 1904. Wright, Phil. Mag. July 1909.

$q$  is due partly to the penetrating rays coming from the active matters contained in the soil, and partly to the presence of the radium and thorium emanations and their successive products of disintegration in the atmosphere.

If  $\gamma_E, \gamma_A$ , and  $\gamma_C$  are the total numbers of ions produced in the whole range by each  $\alpha$ -particle emitted from the radium emanation, radium A, and radium C respectively, and  $\gamma$  their sum, and if  $\gamma_E', \gamma_B'$ , and  $\gamma_C'$  are those for the thorium emanation, thorium B, and thorium C respectively, and  $\gamma'$  their sum \*, then  $q$  is approximately given by

$$q = \lambda_E N_E (\gamma) + \lambda_E' N_E' (\gamma') + q_0,$$

where  $\lambda_E'$  is the constant of transformation of the thorium emanation,  $N_E'$  the number of atoms of the thorium emanation per cubic centimetre of air, and  $q_0$  the number of the negative ions produced per second by the penetrating rays.

Therefore

$$N_{A,+} = \frac{\lambda_E N_E}{\lambda_A + \sqrt{\alpha \sqrt{\lambda_E N_E (\gamma) + \lambda_E' N_E' (\gamma') + q_0}}}$$

is the number of the charged particles of radium A in air in equilibrium, and this must be substituted for  $\frac{\lambda_E N_E}{\lambda_A}$  in the expression for  $Q$ .

From his experiment on a similar subject, Eve† concluded that the collecting distance of a wire raised to  $-10,000$  volts was about 40 to 80 cm. It appears to us more reasonable to introduce the notion of the contributing volume than that of the collecting distance used by him.

#### *Amount of the Emanations present in the Atmosphere.*

(13) We have so far expressed the electric force in terms of the charge per unit length of the wire. If  $-\mu_1$  and  $-\mu_2$  are the charges per unit length of the wires at heights  $h_1$  and  $h_2$  respectively above the ground, then the potential  $V$  at any point is given by the equation

$$V = 2\mu_1 \log \frac{r_1}{r_1'} + 2\mu_2 \log \frac{r_2}{r_2'},$$

where  $r_1$  and  $r_2$  are the distances of the point from the wires respectively, and  $r_1'$  and  $r_2'$  those from the corresponding images of the wires with respect to the surface of the earth.

\* Since 4  $\alpha$ -particles are apparently emitted from the thorium emanation for one from thorium B or C,  $\gamma_1 = 4\gamma_E' + \gamma_B' + \gamma_C'$ .

† Eve, Phil. Mag. July 1905.



Since at the surface of each wire  $V = -11,000$  volts and  $h_1 = 650$ ,  $h_2 = 150$  cm. and the radius of the wires  $= .025$  cm., we have

$$\mu_1 = 480 \quad \text{and} \quad \mu_2 = 560.$$

A simple consideration shows that the expression for  $Q$  for each wire remains the same when there are two wires placed in a vertical plane, as long as  $w_s$  is greater than  $\frac{4\mu k}{.415 \times h}$  cm. per second. Of course, when the potential of each wire is given, its charge  $\mu$  is affected by the presence of the other.

(14) We have, on the other hand, determined the magnitude of the current observed in the electroscope by a method devised by Eve\*, using 6.4 mgs. of radium bromide, which was kindly standardized for one of us by Professor Rutherford, and found that *the unit of the activity we have used corresponds to*

$$4.52 \times 10^{-13} \text{ amp.}$$

(15) Now, when the radioactive equilibrium is established on the wire, the number of atoms of the radium A or that of the radium C breaking up per second per centimetre was

$$\text{shown to be } 4\pi\mu k N_{A,+}, \text{ provided that } w_s > \frac{4\mu k}{.415 \times h}.$$

Suppose that  $l$  cm. of the wire is introduced into the electroscope in the way already described. One half of the  $\alpha$ -particles emitted from the deposit are stopped in the wire itself, and only one half of the remainder are shot out into the space bounded by the cage, and a fraction of the ionization due to these  $\alpha$ -particles is effective in producing a current, as some of the particles travel only a fraction of their range through that space. From the dimensions of the cage and the range of the  $\alpha$ -particles, we have estimated this fraction to be about  $\frac{2}{3}$ , for those emitted from radium C. Assuming that this is  $\frac{2}{3}$ , for the present, the current  $I$  which is observed in the electroscope produced by the ionization due to the radium C will be

$$I = R. 4\pi\mu k. l. e. \gamma_c \frac{\lambda_E N_E}{\lambda_A + \sqrt{\alpha} \sqrt{\lambda_E N_E(\gamma) + \lambda_E' N_E'(\gamma') + g_0}},$$

where  $e$  is the charge on an ion and  $R$  is the ratio of the effective ionization to the total ionization of the  $\alpha$ -particles, and equal to  $\frac{1}{2} \cdot \frac{1}{2} \cdot \frac{2}{3} = \frac{1}{6}$ , as mentioned above.

\* Eve, Phil. Mag. Jan. 1911.

Since the life of the thorium emanation is extremely short, its distribution in the atmosphere will be far from being uniform. However, on the assumption that its amount per unit volume is the same at equal heights, we get similarly the expression  $I'$  for the current due to the thorium deposits, as

$$I' = R' \cdot 4\pi\mu k \cdot l \cdot e(\gamma_B' + \gamma_C') \frac{\lambda_E' N_E'}{\lambda_A' + \sqrt{\alpha} \sqrt{\lambda_E N_E(\gamma) + \lambda_E' N_E'(\gamma') + q_0}},$$

in which  $\lambda_A'$  denotes the constant of transformation of thorium A, and  $R'$  the ratio of the effective ionization to the total ionization of the  $\alpha$ -particles emitted from thorium B and thorium C. At the present stage of accuracy we may

$$\text{put } \frac{R'}{R} = 1.$$

As is seen from (a) and (d), Art. 3,

$$I = 4.06 \times 4.52 \times 10^{-13} = 1.84 \times 10^{-12} \text{ amp.},$$

$$I' = 1.08 \times 4.52 \times 10^{-13} = .49 \times 10^{-12} \text{ amp.},$$

for the upper wire, and

$$I = 4.28 \times 4.52 \times 10^{-13} = 1.93 \times 10^{-12} \text{ amp.},$$

$$I' = 2.20 \times 4.52 \times 10^{-13} = .99 \times 10^{-12} \text{ amp.},$$

for the lower, on the average.

Calculating from the values of these and  $\mu$ 's and the following data:—

$$\begin{aligned} \gamma_E &= 1.74 \times 10^5 *, & \gamma_E' &= 2.02 \times 10^5 \dagger, \\ \gamma_A &= 1.87 \times 10^5 *, & \gamma_B' &= 1.91 \times 10^5 \dagger, \\ \gamma_C &= 2.37 \times 10^5 *, & \gamma_C' &= 2.27 \times 10^5 \dagger, \\ \lambda_E &= 2.08 \times 10^{-6} \text{ (sec.}^{-1}\text{)}, & \lambda_E' &= 1.31 \times 10^{-2} \text{ (sec.}^{-1}\text{)}, \\ \lambda_A &= 3.85 \times 10^{-3} \text{ (sec.}^{-1}\text{)}, & \lambda_A' &= 1.8 \times 10^{-5} \text{ (sec.}^{-1}\text{)}, \\ l &= 2,000 \text{ cm.}, & e &= 4.65 \times 10^{-10} \text{ E.S. units } \ddagger, \\ k &= 1.3, & q_0 &= 2.5 \S, & \alpha &= 3420 e = 1.60 \times 10^{-6} \parallel, \end{aligned}$$

\* Geiger, Proc. Roy. Soc. vol. lxxxii. July 1909.

† These values are obtained by inter- and extrapolation from the values of  $\gamma_E$ ,  $\gamma_A$ , &c.

‡ Rutherford and Geiger, Proc. Roy. Soc. vol. lxxxi. p. 162 (1908).

§ This is the value calculated by Eve (Phil. Mag. Jan. 1911) from the data found by Wright (Phil. Mag. Feb. 1909).

|| We have, for the present, taken the value of Townsend for dust-free air (Trans. Roy. Soc. vol. lxxxi. p. 170).

we obtain

$N_E = 0.090$ , at the height of the upper wire, and

$N_E = 0.082$ , at that of the lower ;

$\frac{N_E}{N_E'} = 13,000$ , for the effective region of the upper wire,  
i. e., in the vicinity of the height of 6.5  
metres above the ground, and

$\frac{N_E}{N_E'} = 6,500$ , for that of the lower wire, i. e., in the  
vicinity of the height of 1.5 metres.

The greater value of  $N_E$  corresponding to the upper wire implies that the condition  $ws \geq \frac{4\mu k}{.415 \times h}$  has not been quite satisfied during exposure. Taking a roughly estimated correction due to this cause into account, we find

$$N_E = \text{about } .1.$$

### Discussion of the Results.

(16) The amount of the radium emanation in the atmosphere is to be directly measured, either by absorption in coconut charcoal or by condensation at the temperature of liquid air, as has been done by Eve\*, Ashman†, and Satterly‡. Their results are shown below.

TABLE II.

Observer.	Average amount of radium emanation per cubic metre.	Ratio of the extreme values.	Locality.
Eve .....	$60 \times 10^{-12}$ curies	7 : 1	Montreal
Ashman .....	$89 \times 10^{-12}$ „	4.4 : 1	Chicago
Satterly .....	$105 \times 10^{-12}$ „	10 : 1	Cambridge

Taking the mean of the above three, the average amount of the emanation in the air near the earth's surface becomes

$$83 \times 10^{-12} \text{ curie per cubic metre,}$$

which corresponds to about 1.4 atoms of the emanation per c.c., i. e., about 14 times the value we have calculated.

\* Eve, Phil. Mag. Oct. 1908.

† Ashman, Amer. Journ. Sci. vol. xxvi. (1908).

‡ Satterly, Phil. Mag. Oct. 1908 and July 1910.

As the direct measurement of the emanation content of the air at Tokyo is at present lacking, it is difficult to assert that  $N_E$  is actually smaller here than at the places above mentioned. From the fairly good agreement of the three observations made at the widely different parts of the earth's surface, it might be thought that its value at this locality would be also of magnitude of the order of 1.4.

(17) There are certainly some errors in the calculation, as, in the actual case, the wires were stretched between the posts quite near the building, and the direction of wind was not always horizontal. But errors due to these causes would not be so much as to account for the observed difference.

A view, which naturally suggests itself to reconcile the calculated value to the value 1.4 found at the other places, is that the particles of radium A, like ordinary gaseous ions\*, do not remain the same, but may come into aggregation with dust particles or become nuclei of condensation of water vapour†, before they are transformed into the atoms of radium B.

It would not at present be possible to form a definite idea, in what manner and what rate these changes take place. However, when a large number of chances are considered, the rate at which the particles of radium A change from its initial state of formation into radium A', say, of mobility  $k'$ , would be proportional to the total number  $N$  of the particles of radium A which remain unchanged. Thus considering together the recombination with the negative ions previously discussed, we get

$$\frac{dN}{dt} = -\lambda N,$$

in which  $\lambda$  can be regarded as a constant as long as the atmospheric conditions remain the same.

Since the atoms of radium A are undergoing disintegration, we have, in the equilibrium state,

$$\lambda_E N_E = \lambda_A N + \lambda N = (\lambda_A + \lambda) N, \text{ or } N = \frac{\lambda_E N_E}{\lambda_A + \lambda}.$$

If  $k'$  is very small compared with  $k$  or 1.3, the expression

\* Langevin, *C. R.* p. 232 (1905); Langevin and Moulin, *Le Radium*, p. 218 (1907); Pollock, *Le Radium*, p. 129 (1909). See also Langevin, *Ann. Chim. et Phys.* p. 289 (1903); Sutherland, *Phil. Mag.* vol. xxxvi. p. 507 (1893), and vol. xviii. p. 341 (1909); Wellisch, *Proc. Roy. Soc.* vol. lxxxii. p. 500 (1909), and *Verh. d. D. Phys. Ges.* p. 159 (1911).

† Rutherford, 'Radioactive Transformations,' p. 207 (1906).

for  $Q$  becomes approximately

$$Q = 4\pi\mu k \frac{\lambda_E N_E^*}{\lambda_A + \lambda} \quad \text{instead of} \quad Q = 4\pi\mu k \frac{\lambda_E N_E}{\lambda_A + \sqrt{\alpha \cdot q}}.$$

The calculated value of  $N_E$  can be brought into agreement with those directly found at the places already referred to by taking  $\lambda$  about 13 times the value of  $\lambda_A$ , or, in other words, if the half-value period of radium A in its initial state be taken about 14 seconds. Of course the value of  $\lambda$  here given only indicates the order of magnitude.

(18) If the last view is correct, the relative amount of the radium and thorium emanations is to be calculated approximately from the following equation

$$\frac{I}{I'} = \frac{\gamma_C}{\gamma_B + \gamma_C} \frac{\lambda_E N_E}{\lambda_E' N_E'} \quad \text{or} \quad \frac{N_E}{N_E'} = \frac{I}{I'} \frac{\lambda_E' \gamma_B' + \gamma_C'}{\lambda_E \gamma_C}.$$

From the average values given in (a) and (d), Art. 3,

$\frac{N_E}{N_E'} = 47,000$  for the upper wire, *i. e.* in the vicinity of the height of 6.5 metres above the ground, and

$\frac{N_E}{N_E'} = 24,000$  for the lower wire, *i. e.* in the vicinity of the height of 1.5 metres.

(19) By making use of a similar formula, W. Wilson† found the relative amount of the two emanations at Manchester to be 37,000. It may be mentioned that the formula used by him had been deduced from Dadourian's assumption‡ that, when the radioactive equilibrium is established on the wire, the number of atoms of the deposit breaking up per second is equal to that of the emanation in that vicinity, which is  $\lambda_E N_E$  according to our notation. Thus there is a fundamental difference between our arguments and those of the latter. It would be evident that  $\lambda_E N_E$  is the number of atoms of the emanation breaking up or that of radium A producing per c.c. of air, but not the number of atoms of the radium A deposited on the wire or that of the radium C breaking up per sec. per cm. of the wire in equilibrium.

(20) Whatever may be the nature of the change in

\* It may be recalled that, in the case of ordinary gaseous ions in the atmosphere, while there are 40 to 50 times as many heavy ions as the small ones, the mobility of the former is only a fraction of one-thousandth of that of the latter. It follows, therefore, that the product of the number present and the mobility for the heavy ions is negligibly small compared with that for the small ones.

† W. Wilson, *l. c.*

‡ Dadourian, *l. c.*

mobility, the theory explains why the variation of the relative amount of the radium deposits on the upper and lower wires,  $\frac{Q_1}{Q_2}$  say, ought to be as observed. According to the calculation,  $\frac{Q_1}{Q_2}$  should be equal to  $\mu_1 : \mu_2 = .87$ , if  $w_s = \frac{4\mu k}{.415 \times h}$ , which is 10.8 cm. per sec. for the upper wire, and 40.0 cm. per sec. for the lower. Therefore, if  $w_s < 40$  cm. per sec.,  $\frac{Q_1}{Q_2}$  will be greater than the above value. In the limiting case, in which there is no wind at all, or the direction of the wind coincides with that of the wire, then  $\frac{Q_1}{Q_2}$  should be  $.87 \times \frac{.75}{.25} = 2.6$ . Consequently, in ordinary circumstances,  $\frac{Q_1}{Q_2}$  will lie between .87 and a value a little greater than that. As is seen from Column IV. Table I., it varied from .90 to 1.01 on different occasions, as is to be expected.

(21) We have already mentioned that the distribution of the thorium emanation in the atmosphere cannot be uniform. Moreover, it is not probable that thorium A having the period of 10.6 hours is in radioactive equilibrium with the emanation *in situ*. Consequently, the ratio of the amounts of deposits on the upper and lower wires or  $\frac{Q_1'}{Q_2'}$  will not be as  $\mu_1 : \mu_2$ , but will vary much with the vertical component velocity of the wind, which is in a fair proportion with the horizontal component velocity. Experiment showed that this was the case.  $\frac{Q_1'}{Q_2'}$  varied within the wide range between .24 and .72, as can be seen from Column VII. Table I. To show the variation of  $\frac{Q_1'}{Q_2'}$  with the velocity of wind, the following figures are taken from the same table.

TABLE III.

Date.	16	17	18	19	19	20	21	23	24	25
$Q_1' : Q_2' \dots\dots\dots$	.24	.56	.57	.67	.72	.62	.31	.38	.44	.48
Order of magnitude ...	10	5	4	2	1	3	9	8	7	6
Mean vel. of wind ...	1.2	3.5	3.6	6.5	10.1	4.8	1.9	3.2	3.1	3.5
Order of magnitude ...	10	6	4	2	1	3	9	7	8	5

We see that the ratio and the wind velocity arrange themselves practically in the same order.

Consequently, the relative ionization of the thorium and the radium types depends on the height at which the wire has been stretched.

*Summary of the Results.*

(a) The decay curves show that the particles of radium A and thorium A are deposited on a negatively charged wire but not other products, such as radium B, radium C, &c.

(b) According to the theory put forward, the number of the particles of radium A deposited per second on unit length of the wire should be a definite quantity, depending on the mobility of the particles, the height of the wire above the ground and its charge per unit length, but not on the velocity of wind, if its component perpendicular to the length of the wire is greater than a certain value.

(c) If the mobility of the particles of radium A be supposed to be constant and equal to 1.3, the average amount of the radium emanation present in the atmosphere at Tokyo should be about

$$5 \times 10^{-12} \text{ curie per cubic metre.}$$

(d) On the assumption that the amount of the thorium emanation per unit volume is the same at equal heights, the ratio of the amount of the radium emanation to that of the thorium is estimated to be

13,000 : 1, in the vicinity of the height of 6.5 metres  
above the ground, on the average, and

6,500 : 1, in that of the height of 1.5 metres.

(e) When we compare the amount of the radium emanation thus obtained with those found at Montreal, Chicago, and Cambridge, we find that the former is much smaller than the latter. If the actual amount of the emanation at this locality be of the same order as that at the places just referred to, we should suppose that the particles of radium A become, while suspending in the atmosphere, heavier particles at a rate much quicker than that at which they are transformed into atoms of radium B.

(f) If this is the case, the ratio given in (d) becomes

47,000 : 1, in the vicinity of the height of 6.5 metres  
above the ground, and

24,000 : 1, in that of the height of 1.5 metres.

(g) A fall in atmospheric pressure seems to have the tendency

of increasing the amount of deposits. This, however, must be due to an increase in the amount of the emanations themselves. It may be added that the range of variation of the amount of the radium deposit observed is practically the same as that of the amount of the emanation observed by Satterly.

In conclusion, we wish to thank Professor Tanakadate for placing the resources of the Laboratory at our disposal, and Professor Nagaoka and the other professors in the Laboratory for their valuable suggestions during the progress of this investigation.

Physical Laboratory, University of Tokyo,  
June 1911.

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LXXXII. *The Solubility of Radium Emanation. Application of Henry's Law at Low Partial Pressures.* By R. W. BOYLE, M.Sc., Ph.D., 1851 Exhibition Science Scholar of McGill University\*.

*Introduction.*

MEASUREMENTS of the solubilities of radium emanation in some common liquids have already been made by a number of experimenters. The results have served to give an approximate idea of the solubility of the gas, but they have in themselves showed such wide variations that no reliance can be placed on any particular figure. The previous determinations were made with the small quantities of emanation such as are measured by means of an ordinary emanation electroscope, that is to say, the equilibrium quantities of about  $10^{-5}$  or  $10^{-6}$  mgm. of radium. The experiments involved more than one transference of emanation to the measuring electroscope, or electroscopes, with the consequent losses of emanation in the conducting and drying tubes.

Since large quantities of radium have become available, the  $\gamma$ -ray electroscope has come to be used for quantitative measurements of emanation. In this method the vessel containing the emanation is simply brought near enough to the electroscope to cause a satisfactory ionization by the  $\gamma$  rays sent out by  $\text{RaCl}_2$ , and this ionization is compared with that produced by a standard quantity of radium at the same distance from the electroscope. The emanation cannot be measured until at least four hours after admitting it into the containing vessel. After this period radioactive equilibrium

\* Communicated by Prof. E. Rutherford, F.R.S.



is established, and the amount of Ra C is proportional to the emanation present.

The simplicity and fair accuracy of the instrument are great advantages, but the chief advantage is that measurements can be quickly and easily taken without actually drawing the emanation into the electroscope. Much time and labour are thereby saved, and there are no corrections to be applied for loss of emanation in the conducting tubes, and in the necessary drying of the gas in which the emanation is contained.

Von Traubenberg was the first to find that radium emanation distributed itself in a definite manner between water and air in contact with one another. From the behaviour of the emanation in experiments which he performed he concluded that the emanation, like other gases, was absorbed by a liquid, and on a basis of the validity of Henry's law he determined the coefficient of absorption or solubility. Henry's law states that the amount of gas absorbed is proportional to the pressure, and from it follows the law of distribution, viz., that the ratio of the concentrations of the gas within and without the liquid is a constant. In this sense the coefficient of solubility is defined as the ratio of these concentrations.

In the case of the radioactive emanations it is, of course, difficult to work without some gas acting as carrier of the emanation, and the coefficient of solubility is defined as follows:—Let a volume of liquid  $v_1$  be in contact with a volume of gas  $v_2$ , and let a quantity of emanation distribute itself between them, so that after equilibrium is established  $e_1$  will be the emanation contained in the liquid, and  $e_2$  that in the gas. Then  $\frac{e_1}{v_1}$  will be the concentration of emanation in the liquid, and  $\frac{e_2}{v_2}$  the concentration in the gas. The ratio of these concentrations, viz.  $\frac{e_1}{v_1} \bigg| \frac{e_2}{v_2}$  is the *coefficient of solubility*.

By Henry's law this ratio, at any one temperature, should be independent of the concentration of the emanation, and of the nature and pressure of the containing gas; it should depend only on the nature of the absorbent. The ratio, however, should decrease as the temperature rises. It is known that Henry's law fails as the liquid approaches saturation. Practically the law only holds for dilute solutions in the case of gases which do not react chemically with the absorbing liquid. These two conditions are fulfilled ideally by radium emanation, and in consequence we should expect

the law to hold exactly. The agreement amongst their own results, which former experimenters must have obtained, is good presumptive evidence that the law is valid; but unfortunately these experimenters differ seriously one from another, and no exact information concerning any one temperature can be taken from their results. For example, the values of the coefficients at ordinary, or room, temperatures are

from Von Trautenberg *	0.33 to 0.36
Mache †	0.30 to 0.33
Hofmann ‡	0.24
Koffler §	0.27 (at 18° C.).

It will be seen later that much depends on what is meant by "ordinary temperature." There is an increase in the coefficient of 25 per cent. while the temperature changes from 18° to 11° C.

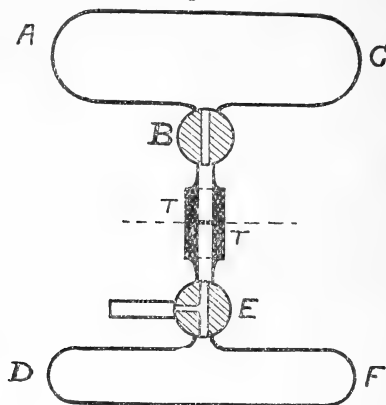
By the methods afterwards described it is easy to put Henry's law to simple and direct test, and to show that in the present conditions it holds exactly. It is desirable that a correct value of the solubility of the emanations in water and a few other liquids should be known, especially over the range of ordinary working temperatures.

#### *Methods of Experiment.*

The solubility may be determined by very simple methods, which may be described as follows:—

ABC and DEF are two bulbs of the same length, but not

Fig. 1.



necessarily of the same diameter. The first bulb is fitted with an ordinary two-way stopcock B, and the second with

\* *Phys. Zeit.* v. p. 130, March 1 (1904). † *Wiener Ber.* cxiii. p. 1329 (1904).

‡ *Phys. Zeit.* vi. p. 337 (1905).

§ *Phys. Zeit.* ix. p. 6 (1908).

a three-way stopcock E. These stopcocks are joined to the bulbs as closely as possible, and the glass tubing connected with each stopcock is only about 1.5 cm. long.

For convenience we shall call the bulb ABC the *mixing* bulb, and DEF the *sampling* bulb.

The volumes of the bulbs and the tubing connected with them must be known. These are conveniently determined by completely filling with mercury at a definite temperature and weighing the mercury.

Before a series of experiments the bulbs were thoroughly cleaned, dried, evacuated, and then weighed. In lubricating the stopcocks as little grease as possible was used. It is essential that the stopcocks should be able to maintain a vacuum in the bulbs, and this point was always tested before experiment.

To perform an experiment the mixing bulb was evacuated, and the emanation to be used was admitted into it. The required amount of absorbing liquid was then forced slowly into the bulb by the pressure of the atmosphere, and air, or other gas, was allowed to fill the bulb to the pressure required. When other gases than air, or air at pressures other than atmospheric, were to be employed as carriers of the emanation, the necessary apparatus for the purpose was constructed and used.

After admitting the emanation and the absorbing liquid into the mixing bulb, both mixing and sampling bulbs were joined together by about two centimetres of very tightly fitting pressure-tubing TT, in the manner shown in the diagram (fig. 1). In order that the joints should be perfectly airtight the pressure-tubing was secured by wire and wax so that when tested the joints showed no leak whatever. The three-way stopcock attached to the sampling bulb was next attached to a Toepler pump, and the interior of the sampling bulb and connexions were exhausted, the stopcock of the mixing bulb still being kept closed. The three-way cock was then closed to the open air and disconnected from the pump, after which the bulbs were placed in a bath maintained at the required temperature of experiment. The manner of connecting the bulbs together made the whole quite rigid, and shaking could be performed by a suitable mechanical contrivance or by hand, whichever was the more convenient.

The temperature bath used in these experiments was a thermostat controlled by a toluol bulb with attached electric relay and electric heating device. Usually the temperatures were constant to  $0^{\circ}1$  C., but sometimes on account of the sticking of the relay there was a larger variation, but never greater than  $0^{\circ}2$  C.

Although the equilibrium distribution of emanation is

quickly established, the bulbs were left in the temperature bath for an hour or more (sometimes as much as two or three hours), and very frequent shakings were given. This length of time in the bath ensured that the absorbing liquid had taken up the proper temperature. After shaking, the bulbs were allowed to stand in the bath for ten minutes, which allowed the bubbles of gas suspended in the liquid to come to the surface.

From this point on an experiment may be proceeded with in one or the other of two ways.

*Method 1.* Holding the bulbs vertically in the bath, with the sampling bulb uppermost, the interiors of the two bulbs are put in connexion by opening the stopcock of the mixing bulb. The gas in this bulb then expands and occupies the free space of the two bulbs together. The two stopcocks are then shut, thus enclosing the contents of the respective bulbs.

*Method 2.* With the bulbs vertical and the mixing bulb uppermost, the stopcock of the mixing bulb is opened, thus allowing the liquid inside it to be forced by the pressure of the gas above into the lower, evacuated, bulb. The volume of the absorbing liquid used should be, preferably, just a little more than the volume of the sampling bulb and connexions, so that the sampling bulb can be completely filled. After this expulsion of liquid both stopcocks are closed.

Both the operations just mentioned take place in a second or two, so that there is no time for the emanation to stream out of the liquid and form a new equilibrium. When the stopcocks are closed, the bulbs are taken from the bath and disconnected by removing the pressure-tubing. The end tubes are dried out with blotting-paper, and the bulbs are set aside for at least four hours, after which their emanation contents are measured by means of the  $\gamma$ -ray electroscope.

The coefficients of solubility are calculated as follows:—

Let  $A$  = vol. of the mixing bulb,

$B$  = vol. of the sampling bulb,

$T$  = total vol. of both bulbs plus their connexions,

$V$  = total vol. of absorbing liquid used,

$v_1$  = vol. of absorbing liquid left in the mixing bulb after the experiment,

$v_2$  = vol. of absorbing liquid found in the sampling bulb after the experiment,

$r$  = the ratio of the emanation in the mixing bulb to that in the sampling bulb after the experiment,

$c$  = the emanation per c.c. of the gas in the mixing bulb before expansion,

$S$  = the coefficient of solubility.

*Method 1.* In the mixing bulb  $V$  is the volume of the liquid, and  $A-V$  the volume of the gas. After equilibrium there will be  $(A-V)c$  units of emanation in the gas and  $VcS$  in the liquid. The gas is expanded from a volume of  $A-V$  to a volume of  $T-V$ , so that the density is reduced in the ratio  $\frac{A-V}{T-V} = K$ .

Therefore, on closing the stopcock there will be in the mixing bulb  $(A-v_1)kc$  units of emanation in the gas, and  $v_1cS$  in the liquid. Hence the total emanation in this bulb equals  $(A-v_1)kc + v_1cS$ .

Similarly, the emanation carried by the gas into the sampling bulb will be  $(B-v_2)kc$ , and by possible small drops of liquid which have been blown over into this bulb  $v_2cS$ . The total equals

$$(B-v_2)kc + v_2cS.$$

Since the ratio of the emanation in the two bulbs equals  $r$  we have

$$\frac{(A-v_1)k + v_1S}{(B-v_2)k + v_2S} = r, \quad . \quad . \quad . \quad . \quad (1)$$

the  $c$  cancelling out. From this formula  $S$  can be calculated. As an example a determination at  $14^\circ \text{C}$ . is given; the following are the data:—

$$A = 33.18 \text{ c.c.}$$

$$B = 18.87 \quad ,,$$

$$V = 18.72 \quad ,,$$

$$v_1 = 18.66 \quad ,,$$

$$v_2 = 0.03 \quad ,,$$

$$k = 0.430$$

$$r = 1.456$$

$$\text{Therefore } S = 0.299.$$

*Method 2.* In this method, although the expulsion of liquid causes the gas in the mixing bulb to expand, all of it remains in the bulb. Therefore, on closing the stopcock there will be in this bulb  $(A-V)c$  units of emanation in the gas, and  $v_1cS$  in the liquid. The total will be  $(A-V)c + v_1cS$ .

The emanation going to the sampling bulb will simply be  $v_2cS$ . Hence in this case

$$\frac{(A-V) + v_1S}{v_2S} = r. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For example, in a determination at  $14^{\circ}\text{C.}$ ,

$$A = 33.18 \text{ c.c.}$$

$$V = 12.2 \quad "$$

$$v_1 = 1.29 \quad "$$

$$v_2 = 10.73 \quad "$$

$$r = 6.50$$

$$\text{Thus } S = 0.306.$$

In Method 1, without very appreciable errors,  $v_1 = V$ ,  $v_2 = 0$ , and  $T = A + B$ ; similarly, in Method 2  $v_2 = B$ . The ratio  $r$  must be measured very correctly for use in the formulæ above, more especially in formula 1, where differences appear in the numerator and denominator of the expression for  $S$ . The quantities  $V$ ,  $v_1$ , and  $v_2$  can be quickly and conveniently determined by separately weighing the bulbs before and after placing them in the temperature bath, and subtracting the respective weights of the empty bulbs. The specific gravities of the absorbing liquids must be known or must be determined.

*Method 1*—the sampling of the gas-phase—is more suitable when the gas takes a greater share of the emanation than the liquid, that is, generally speaking, when the coefficient is less than unity. This is the case of water and of aqueous solutions of salts.

*Method 2*—the sampling of the liquid-phase—is better used when the liquid takes the greater amount of emanation. This is the case of many organic liquids. By choosing the more suitable method, errors due to the mechanical suspension of drops of liquid in the gas-phase, or of bubbles of gas in the liquid-phase, may be minimized. Also, after a few trial experiments, it is possible so to select the sizes of the bulbs and the amount of absorbing liquid as to have nearly the same quantity of emanation in both mixing and sampling bulbs. This makes it possible to obtain nearly equal rates of movement of the gold-leaf in the electroscope, and thus avoid possible instrumental errors.

In the case of water below ordinary temperature, the two methods agree very well, as is shown in the examples already given, and in the following which refer to  $0^{\circ}\text{C.}$  :—

By Method 1.

$$A = 37.21 \text{ c.c.}$$

$$B = 25.76 \quad "$$

$$V = 18.60 \quad "$$

$$v_1 = 18.55 \quad "$$

$$v_2 = 0.02 \quad "$$

$$k = 0.416$$

$$r = 1.585$$

$$\therefore S = 0.500$$

By Method 2.

$$A = 33.17 \text{ c.c.}$$

$$V = 20.39 \quad "$$

$$v_1 = 9.22 \quad "$$

$$v_2 = 10.81 \quad "$$

$$r = 3.17$$

$$\therefore S = 0.511.$$

*Precautions and Errors.*

A few preliminary experiments showed that the solubility varied with temperature more markedly than former results led one to suppose. They also showed that equilibrium of the emanation between the water and gas-phases was fairly quickly established. If the admixture of gas and liquid by shaking is effective, as it must be with bulbs of the shape shown, it is necessary to wait only a few minutes after the absorbent has taken up the temperature of the bath. In one series of experiments shaking was carried on for 8 and for 24 minutes; the same results were obtained for the coefficient as when the mixing bulb was left in the bath for 18 hours.

In order to secure good  $\gamma$ -ray observations the mixing and sampling bulbs should not be too large. The mixing bulbs used in the experiments were of volumes 37.22, 33.18, and 26.01 c.c.; the sampling bulbs of 25.77, 24.98, 18.87, and 10.97 c.c. respectively. The length of the bulbs was 8 cm. Any one of the mixing bulbs could be used with any one of the sampling bulbs as experiment required.

In taking the  $\gamma$ -ray measurement four observations of ionization were taken for each bulb, viz. when the stopcock was vertically above and also vertically below the bulb, and the same when the bulb was reversed. In laying aside the bulb to wait for radioactive equilibrium they were always placed so that the stopcocks hung vertically below the bulb; this ensured a symmetrical distribution of the active deposit. If this precaution is not attended to, but a bulb containing liquid is left lying on its side, there will be less Ra C on the part of the wall in contact with the liquid than on the opposite part in contact with the gas. When the  $\gamma$ -ray observations are taken this difference will cause, if the distance from the electroscope is small, a discrepancy in ionization readings on reversal of the bulb.

There is always a slight error which is caused by the small absorption of  $\gamma$  rays in the liquid contained in a bulb; but the error is very small, and in these experiments is certainly less than half of one per cent. The  $\gamma$ -ray readings varied a little less than one per cent. between extremes, and they were always corrected, so that the emanation contents of both mixing and sampling bulbs referred to the same time.

The experiments are liable to an error due to the suspension of small bubbles of gas in the liquid. This error affects the measurements of solubility of any gas in any liquid, and to a certain extent cannot be avoided. The lubricant used on the

stopcocks is to some extent an absorbent of the emanation, but the extremely small amount of it exposed to the emanation in these experiments could not have been the cause of any appreciable error.

On the whole the accuracy expected was about 1·5 per cent., and this is about the range of agreement shown in the results given later.

The fact that the emanation produces small quantities of hydrogen and oxygen by its action on water, and that the  $\alpha$  rays produce ozone, should not affect the results. It will be shown that the nature of the gas, or mixture of gases, holding the emanation has no effect on the coefficient, at least within the experimental error. It might be remarked that when air or oxygen was used as holder of the emanation there was a very strong odour of ozone on opening the bulbs.

In the different experiments with distilled water, the results of which now follow, the ratio of volume of water to volume of gas within the mixing bulb varied between 0·5 and 2·5.

## RESULTS.

### (1) *On Henry's Law.*

The experiments to show the constancy of the coefficient of solubility were carried out at 14° C., using air as the gas holding the emanation.

It was found that with the same pressure of air but different concentrations of emanation, or with different

TABLE I.  
Temperature 14° C.

Pressure of containing Gas in cm. Hg.	Concentration. Emanation per c.c. of gas.	Coefficient of solubility.
183	1·81 millicuries *	0·301
145	0·076	0·299
81·6	0·41	0·300
76·0	1·44	0·300
62·0	0·017	0·309
36·8	0·21	0·303
14·7	0·20	0·307
9·0	0·041	0·302

\* [The *curie* is defined (following the suggestions of the Brussels Conference) as the quantity of emanation in radioactive equilibrium with one gram of radium element. One millicurie is 1/1000 of this unit.]



pressures of air and about the same concentration of emanation, the same values of the coefficient were obtained within the error of experiment. Table I. gives a number of results showing that pressure and concentration of emanation can be changed together without altering the result. Most of the experiments were carried out by Method 1 described further back, but a few were by Method 2.

In the above the coefficient remained constant within experimental error, although the air-pressures varied from 183 to 9 cm. Hg, a ratio of 20 to 1, and the concentrations varied irregularly from 1.81 to 0.017 millicuries per c.c., a ratio of 108 to 1.

It will be noticed in Table I. that with one or two exceptions the coefficients appear to be lowest in the case of the highest pressures. This is probably accidental, and no special inference can be drawn, since the values shown do not differ from the mean by more than the experimental error.

With regard to the concentrations mentioned above, it is interesting to calculate the partial pressures of emanation they denote. The volume of 1 curie of emanation is 0.6 cubic mm. at N.T.P. Assuming Boyle's law, the above concentrations mean a variation of partial pressure of emanation from 0.0008 mm. Hg to 0.000008 mm. Hg. Taking the number of molecules per c.c. of a gas at atmospheric pressure to be  $2.8 \times 10^{19}$ , these concentrations are equivalent to a variation from  $3 \times 10^{13}$  to  $3 \times 10^{11}$  molecules of emanation per c.c. With any ordinary gas it would be impossible to perform corresponding experiments at such extreme tenuity.

Experiments were also performed with other gases containing the emanation. Since the attraction by the small mass of a gas is not comparable with that of the greater mass of a liquid no differences in the coefficient should be found provided that the gas does not change materially the nature of the absorbent. The results of one experiment with each gas are given in Table II.

TABLE II.  
Temperature 14° C.

	Gas.	Pressure.	Coefficient.
Pure Gases	Oxygen	80 cm. Hg	0.304
	Hydrogen	36    "	0.308
	Carbon dioxide	77    "	0.307
Mixtures	Coal gas	76    "	0.306
	Coal gas and air	76    "	0.299

This table shows that the coefficient remains constant, within experimental error, although the nature of the gas is completely changed. Both tables show definitely that Henry's law is valid.

(2) *The Variation of the Solubility with Temperature.*

Experiments were carried out with air and distilled water from 0° C. to 39°·1 C., the air containing the emanation being at atmospheric pressure. At about 50° C. and higher the same methods cannot be used, on account of the running of the lubricant of the stopcock and breaking down of the vacuum. The chief essential of the experiments is that the vacuum in the sampling bulb should be maintained during an experiment, otherwise the values obtained for the coefficient would be too high. The results are shown in Table III., which gives only the means for the different temperatures, but the range of temperature was traversed twice.

TABLE III.

Temperature.	Coefficient.	Temperature.	Coefficient.
0° C.	0·506	17·6° C.	0·280
4·3	0·424	20·0	0·245
5·7	0·398	26·8	0·206
10·0	0·340	31·6	0·193
14·0	0·303	34·8	0·176
		35·2	0·170
		39·1	0·160

From the figures of Table III. the solubility-temperature curve is plotted and shown in fig. 2 (p. 851). The variation with temperature is quite marked, and does not agree with the former results published by Hofmann\*.

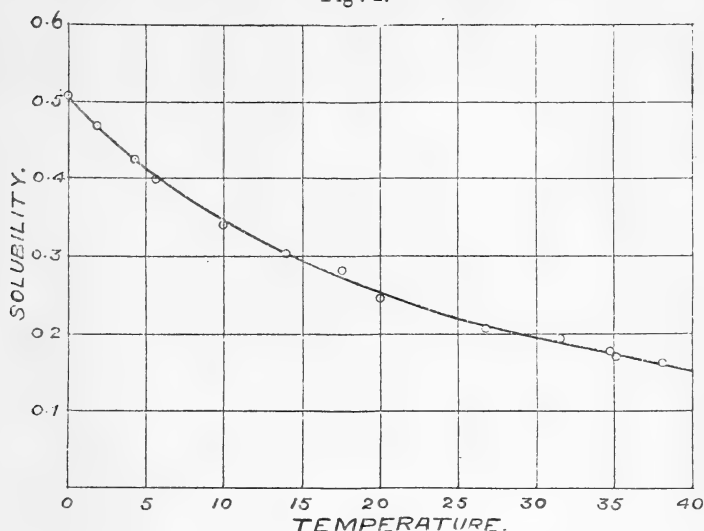
(3) *The Solubility in other Liquids.*

The solubilities in a few organic liquids were measured. In these cases stopcocks could not be used, for the liquids dissolve the tap grease and thus cause the bulbs to leak. In consequence, light pressure-tubing with screw-clips was used instead of stopcocks. The tubing was secured to the bulbs by wire and the joints were waxed so that on testing the bulbs were quite airtight. A three-way tap, held between

\* *Loc. cit.*

the bulbs by the pressure-tubing, allowed exhaustion of the sampling bulb previous to an experiment.

Fig. 2.



In the case of these organic liquids, which absorb the emanation so strongly, the better method to use is Method 2, previously described. Possibly, on account of the use of rubber tubing instead of stopcocks, the results are not quite so accurate as those in the case of water; the error, if anything, would make the results a little too high. The solubilities are given in Table IV., and refer to 14° C.

TABLE IV.

Liquid.	Sp. Gr. at 14° C.	Coefficient of solubility.	Absorbing power compared with that of water at 14° C.
Absolute alcohol ..... $C_2H_6O$	0.796	7.34	24.2
Amyl alcohol ..... $C_5H_{12}O$	0.817	9.31	30.7
Toluol ..... $C_7H_8$	0.871	13.7	45.2

These figures suggest the probability that there are some organic liquids which absorb the emanation even more

strongly than toluol; higher members of the benzene series, for instance, might be examples.

Determinations of the coefficient were also made with mercury and with sea-water. It was desired to find if the former absorbed, or occluded, the emanation to any appreciable extent, and measurements on the latter had a bearing on the values of natural ionization found over the ocean and the disparity between these values and those over the land.

The observations with mercury showed that it does not absorb the emanation to an appreciable extent, and that in the experiment any emanation which was mechanically suspended in the mercury was not enough to be detected within the error of experiment. When the  $\gamma$ -ray measurements were made care was taken not to disturb the mercury in the bulb from the position it had when the bulb was laid aside to wait for radioactive equilibrium. This prevented the occlusion of some of the Ra C in the mercury, and the consequent appreciable absorption of  $\gamma$  rays by the latter.

The sample of sea-water experimented on was taken from a river estuary in Wales; its specific gravity at  $14^{\circ}$  C. was 1.022. The value obtained for the coefficient (one determination) was 0.255. This is a very appreciable absorption, and its value must have a bearing on the results obtained for the natural ionization and amount of radioactive products in the atmosphere, over the ocean and over the land. Both these quantities vary between very wide limits; but it is certain that, on an average, they are less over the ocean than over the land. The facts have been well brought out in a recent paper by Simpson and Wright\*, who showed in addition that generally the natural ionization and the amount of radioactive products increased as land is approached from mid-ocean. The natural ionization is to some extent dependent on the quantity of radioactive products, and this latter to some extent on the amount of radium emanation present. On account of the absorbing power of the ocean there should be less emanation per unit volume of air over the ocean than over the land, whence the greater part of the emanation is supplied; and for the same reason this quantity of emanation should increase as land is approached from mid-ocean. Probably this is not the only explanation for the disparity mentioned, but certainly it is a contributing effect.

\* Proc. Roy. Soc. A. lxxv. p. 175 (1911).

*Conclusion.*

Within the limits of experiments previously stated, it is found that in the case of radium emanation Henry's law is valid. In comparison with many ordinary gases the emanation may be considered fairly soluble.

It is interesting to compare the solubility of the emanation in water with that of some common gases, adopting the same definition of the coefficient of solubility as above. The following table shows approximate values which refer to the condition of an atmosphere of the gas in question pressing on the surface of the absorbing liquid. The temperature chosen is 14° C.

Gas.	Coefficient of solubility.
Hydrogen .....	0.02
Nitrogen .....	0.02
Oxygen .....	0.04
Ethylene .....	0.17
Nitric oxide .....	0.28
Nitrous oxide.....	0.81
Carbon dioxide .....	1.1
Sulphuretted hydrogen	3.3

For emanation, the coefficient at 14° C. is 0.303, and it decreases from 0.507 at 0° to 0.153 at 40° C.

At 14° C. a quantity of emanation will distribute itself between equal volumes of water and a gas so that about one-quarter will go to the water and three-quarters to the gas. At 0° C. one-third will go to the water and two-thirds to the gas.

Of the other liquids examined it is found that mercury does not absorb the emanation, and that sea-water of specific gravity 1.022 at 14° C. absorbs about 0.84 times as strongly as water. Organic liquids absorb very strongly. At 14° C. ethyl alcohol (absolute) absorbs 24 times, amyl alcohol 31 times, and teluol 45 times as strongly as water.

The interest of experiments such as the above is not confined entirely to considerations of radioactivity. The experiments described were performed on a gas at partial pressures of from  $8 \times 10^{-4}$  to  $8 \times 10^{-6}$  mm. Hg, and it was found that under these conditions one of the ordinary gas laws holds good. At these extreme tenuities, researches on the physical and physical-chemical properties of gases by all other methods are barred to us by experimental limitations.

The present experiments are an illustration of the fact that by using the emanation of radium, researches on gaseous properties may be carried into new regions; and work, quite impossible with ordinary gases, becomes practicable and easy by virtue of the very simple and convenient property of ionization.

The writer wishes to express his indebtedness to Professor Rutherford for the very frequent supplies of emanation, and also for his very helpful interest and advice.

University of Manchester,  
July 1911.

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LXXXIII. *The Difference in the Photoelectric Effect caused by Incident and Emergent Light.* Part II. By OTTO STUHLMANN, Jr., M.A., *Experimental Science Fellow, Princeton University*\*.

*Introduction.*

**I**N a previous communication † the writers showed that when a beam of ultra-violet light, from an iron arc, impinges on a film of platinum so thin that its absorption can be neglected, the photo-electric effect caused by the emergent beam is greater than the photo-electric effect caused by the incident beam.

Thus for platinum sputtered from a cathode on quartz plates *in vacuo*, the ratio of the emergent photo-electric effect to the incident photo-electric effect was as 1.17 to 1.0, when the absorption of the millimetre quartz plate on which the platinum film was mounted was allowed for.

Shortly after a preliminary account of part of the matter described in the above paper had been published ‡, a notice appeared in 'Nature' by R. D. Kleeman §, who also found that this want of symmetry between the emergent and incident photo-electric effect existed when ultra-violet light fell normally on thin films of platinum sputtered *in vacuo*. By using a rather thick sputtered film of the metal which allowed only 55 per cent. of the incident light to pass through, he found that the ratio of the emergent to the incident photo-electric effect was as 1.15 is to unity, without

\* Communicated by Prof. O. W. Richardson.

† O. Stuhlmann, Jr., *Phil. Mag.* xx. p. 331, Aug. 1910.

‡ *Nature*, May 12, 1910.

§ *Nature*, May 19, 1910. Also later *Proc. Roy. Soc. A.*, vol. lxxxiv. (1910).

allowing for the absorption of the film and the 0.3 mm. quartz plate on which the film was mounted.

Had thinner films of platinum been used and allowance been made for the absorption of the light by the quartz, I find that his value would have increased from 1.15 to unity to 1.17 to unity for the ratio of the emergent to the incident photo-electric effect. He repeated his experiments *in vacuo* and found that they checked his previous values when air at atmospheric pressure was in his apparatus.

In view of this work it was thought unnecessary to repeat the above experiments *in vacuo*, since as they stand they are confirmed by Kleeman's results. His measurements were made by an electroscope method which is quite different from the one used in this investigation.

Some years ago Hallwachs\* showed that a photo-electric effect could be obtained with a silvered quartz plate when the light was incident through the quartz. This he suggests can be explained in two ways: either the light passes through the silver and liberates electrons at the rear surface of the metal, or the electrons acted on by the light at the incident surface have velocities great enough to carry them out through the rear side. A similar effect was found by Rubens and Ladenburg† with gold-leaf.

They found that the ratio of the photo-electric effect in front and behind was 100 to 1.0, while the fraction of the ultra-violet light transmitted, photo-electrically measured, was one one-thousandth. That they did not and could not have foreseen that the emergent photo-electric effect was greater than the incident effect has been pointed out by Kleeman‡.

The object of the present investigation is to determine the magnitude of the ratio of the emergent to the incident photo-electric effect for as many characteristically different metals as practicable. In this connexion the phrase photo-electric effect is to be understood as the total electronic emission due to light of standard intensity.

#### *Method of Experimenting.*

The same apparatus and method of experimenting was used as in the first paper on this subject§. A beam of ultra-violet light from an iron arc was passed along the common

\* Hallwachs, *Tagbl. d. Heid. Nat. Ver. S.* 24 (1890).

† Ladenburg, *Deutsch. Phys. Gesell. Verh.* ix. p. 24, § 749-752 (1907).

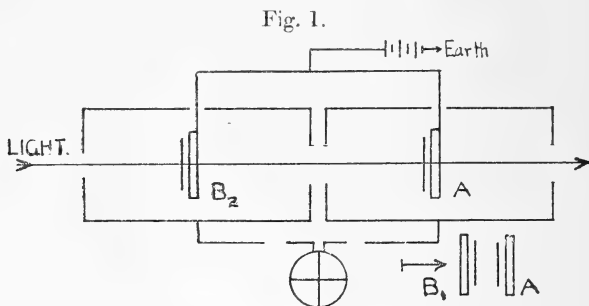
‡ *Loc. cit.*

§ O. Stuhlmann, Jr., *Phil. Mag.* xx. p. 333, Aug. 1910.

axis of two brass cylinders placed horizontally end to end. These were insulated from their supports by quartz stays. In the centre of each cylinder perpendicular to the ray, a quartz plate one millimetre in thickness was suspended and was covered on one of its faces with a thin film of the metal under investigation, obtained by sputtering from a cathode *in vacuo*. The films were maintained at a constant negative potential of 200 volts. Each cylinder was connected to one set of quadrants of a Dolezalek electrometer giving 716 divisions deflexion per volt at a scale distance of one metre, with a constant potential of 80 volts on the needle.

It may be of interest to add that a phosphor-bronze strip suspension was used in the electrometer. Any desired sensitiveness could be obtained by gradually reducing the breadth and thickness of the strip by dissolving it away with dilute, warm nitric acid.

The tandem arrangement of mounting the plates (see fig. 1) allowed one to use a differential method. It consisted in measuring for various thicknesses of metal films the saturation current for two successive positions of the plates.



The plate A was always maintained stationary with the film side facing the light. The second plate could be rotated about a vertical axis so that the film successively faced towards the light (B<sub>2</sub>) and away from the light (B<sub>1</sub>).

In the first case the ratio of the ionization  $\frac{B_1}{A}$  was measured, giving the ratio of the emergent effect at B to the incident effect at A. In the second case the ratio  $\frac{B_2}{A}$  was obtained, giving the ratio of the incident effects for the two plates. Hence the ratio  $\frac{B_1}{A}$  to  $\frac{B_2}{A}$  gave the value of the ratio of the emergent effect to the incident effect at the same plate B.



This method avoids any difficulties which might be caused by fluctuations in the illumination.

The absorption of the thinnest films became a negligible quantity because the ratio  $\frac{B_1}{B_2}$ , when plotted against the thickness of the films, approached a limiting value as the thickness was indefinitely diminished. Hence the limiting value corresponds to the case in which the value  $\frac{B_1}{B_2}$  arises from a true difference in the ionization produced by emergent and incident light of equal intensity.

### Data.

The metals investigated for the difference in the photo-electric effect caused by the incident and the emergent light include magnesium, copper, zinc, silver, tin, platinum \*, lead, and iron. In addition selenium, arsenic, and carbon gave unsatisfactory results. Selenium could not be sputtered *in vacuo* owing to its low melting-point. The cathode became distorted, in consequence of heating by the current, before any satisfactory films could be deposited. Carbon gave very satisfactory films of uniform texture, but its photo-electric activities are so small that the results became worthless owing to the fact that the magnitude of the results was never greater than the experimental error.

The above metals were chemically pure and were supplied by Kahlbaum, Berlin, except silver which was commercial "Fine Silver," and was supplied by a local firm.

It was desirable wherever possible to test such metals as exhibited the most diverse chemical and physical properties. Here one is limited by the possibility of sputtering, rapidity of oxidation, lack of photo-electric response and rapidity of fatigue.

The values of the ratios  $\frac{B_1}{A}$  and  $\frac{B_2}{A}$  obtained for a series of films of different thicknesses and for the metals cited above, are given in the following tables. The third column headed  $\frac{B_1}{B_2}$  gives the ratio of  $\frac{B_1}{A}$  to  $\frac{B_2}{A}$  or the ratio of the emergent photo-electric effect to the incident effect at the same film. The last column gives the values of  $\log \frac{B_2}{A}$ , which is proportional to the optical thickness of the film plus that of the quartz plate used, as was shown in the first paper on this subject.

\* For data on platinum see pt. i. *loc. cit.*

858 Mr. Otto Stuhlmann on *Difference in Photoelectric*  
Magnesium.

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.00	.99+	1.01	.000
1.06	1.02	1.04	.008
1.24	1.19+	1.04	.078
1.15	1.19	.965	.075
1.37	1.32	1.03	.121
1.27	1.34	.948	.127

Copper.

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.09	1.07	1.02	.030
1.23	1.17	1.05	.068
1.31	1.24	1.05	.093
1.28	1.24	1.03	.093
1.33+	1.29	1.03	.111
1.31	1.34+	.974	.129
1.37	1.34+	1.02	.129
1.41	1.37	1.03	.137
1.46	1.43	1.02	.155
1.38+	1.54	.904	.188
1.23	1.71	.718	.233
1.25	1.71	.730	.233
1.29	1.76	.732	.246
1.23	1.78+	.689	.252

Zinc.

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.20	1.13	1.06	.053
1.33+	1.25+	1.06+	.096
1.38	1.35	1.02	.130
1.45	1.37	1.06	.137
1.52	1.45	1.05	.162
1.71	1.68	1.02	.225
1.53	1.74	.879	.241

Silver.

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.18	1.20	.985	.079
1.35	1.33	1.01	.124
1.42	1.41	1.00	.149
1.64	1.66	.987	.220
1.62	1.68	.961	.225

Tin.

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.26+	1.16	1.09	.064
1.30	1.20	1.08	.079
1.35	1.21	1.11	.083
1.31	1.20	1.09	.079
1.37	1.29	1.06	.110
1.57	1.43+	1.09	.157
1.65	1.48+	1.11	.171
1.71	1.56	1.09	.193
1.74	1.57	1.11	.196
1.80	1.68	1.07	.225
1.90	1.67+	1.13	.225
1.87	1.68+	1.11	.227
1.81	1.73	1.05	.238
1.79	1.82	.984	.260

Lead.

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.12	1.07	1.04	.029
1.23	1.12	1.10	.049
1.19	1.14+	1.04	.057
1.32+	1.24	1.07	.093
1.38	1.25	1.10	.097
1.50	1.51	.995	.179
1.53	1.69	.905	.228

$B_1/A.$	$B_2/A.$	$B_1/B_2.$	Log $B_2/A$ proportional to thickness of film.
1.14	1.18	.967	.072
1.21	1.23	.983	.089
1.25	1.28	.976	.107
1.25	1.30	.961	.113
1.26	1.31	.962	.117
1.22	1.45	.841	.161

Fig. 2.

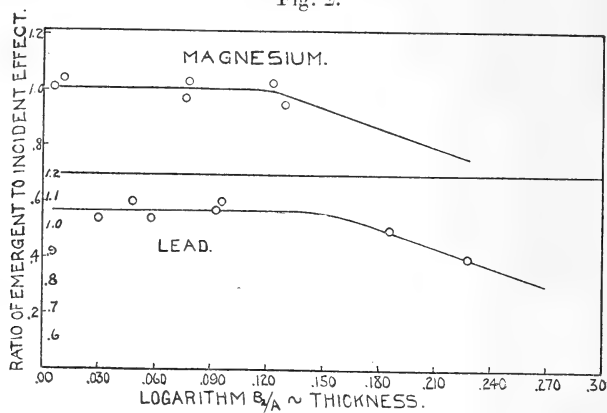
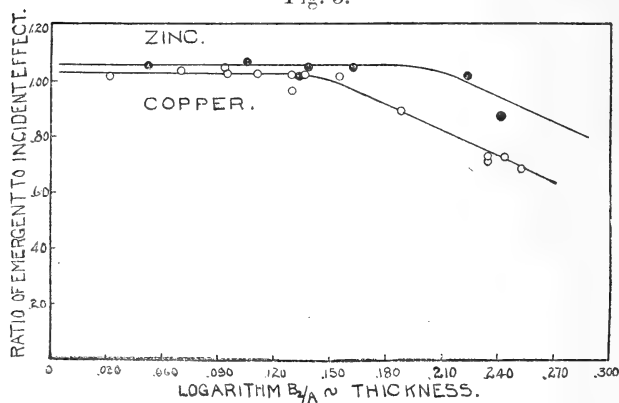


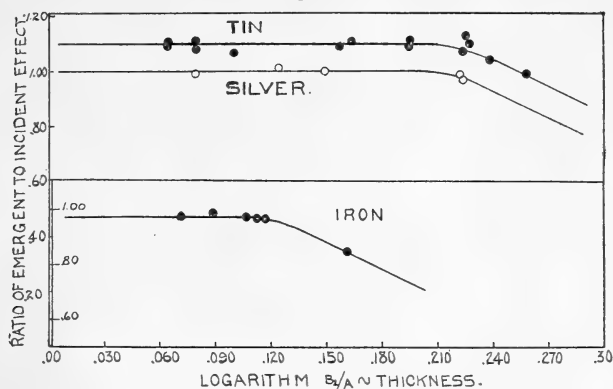
Fig. 3.



Hence a graph (see figs. 2, 3, 4) of the ratio of the emergent

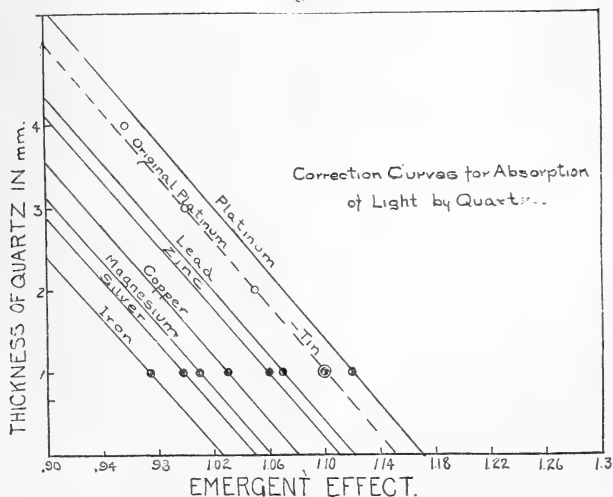
to the incident effect plotted against  $\log B_2/A$  will be identical in form with that plotted against thickness.

Fig. 4.



It is seen that all the curves possess a common form, such that, as the metal decreases in thickness the emergent beam gradually becomes more prominent in its effect, until a certain thickness is reached where the ratio of the emergent to the incident effect attains a constant value. To this constant value must be added the absorption due to the millimetre

Fig. 5.



quartz plate upon which the metal films are mounted. The corrected values thus obtained \* are given in fig. 5.

\* For method and data see pt. i. *loc. cit.* p. 338.

The correction curve for tin and the original or uncorrected curve for platinum, upon which experiments were carried on to determine this absorption of the ultra-violet light by the quartz, happen to give identical values. The broken line is here used to call attention to the fact that the original uncorrected curve for platinum and the correction curve for tin are identical.

### *Conclusions.*

If the metals are arranged in the order of their atomic weights and also according to their position in the periodic system as given in the table below, one notices that there is a periodic increase in the ratio of the emergent to the incident photo-electric effect as one ascends through the periods of the table.

	Metal.	Emergent Photo Effect.	At. Wt.	<u>Effect.</u> <u>At. Wt.</u>
II. Period .....	Mg	1.06	24.4	435
III. Period .....	Fe	1.02+	55.9	183
IV. Period .....	Cu	1.08	63.6	170
	Zn	1.11	65.3	170
VI. Period .....	Ag	1.07	107.9	99
	Sn	1.15	118.5	97
VIII. Period .....	Pt	1.17	194.8	60
IX. Period .....	Pb	1.12	206.9	54

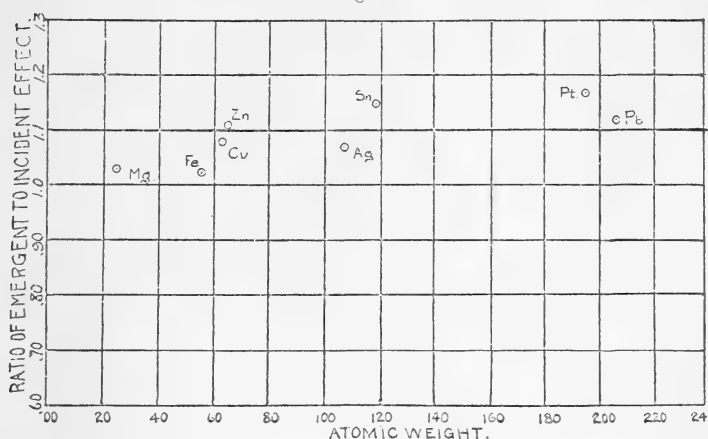
This becomes more apparent when the values for the ratio of emergent to incident photo-electric effect are plotted against their atomic weights as in fig. 6.

Iron, although of a higher atomic weight than magnesium, has a smaller forward effect. The increase in atomic weight from zinc to silver is large, yet the forward effect of silver has very much decreased. The increase in the effect from copper to zinc is about the same as that from silver to tin, while the value for lead, three periods removed, drops to a value nearly equal to that of zinc in the fourth period.

This seemingly points to a periodic variation of the forward effect with the change in the atomic weight, and likewise to a more rapid variation at the end than at the beginning of a period. In the last column of the above table the ratio of the effect to the atomic weight has been tabulated. It will

be observed that the ratio has a constant value in each period. One cannot, however, feel certain that this is a universal law,

Fig. 6.



since it has only been possible to test it in the case of two groups with two elements in each group. Moreover the ratio of the emergent to the incident effect never differs much from unity and there is no very great difference in the values of the atomic weights of the elements in a given group. Thus the range of possible variation is rather restricted.

Since it is known that the incident photo-electric effect increases with decreasing wave-length of the incident light, it may be that the ratio of the emergent to the incident effect would be constant for monochromatic light, so that the present variations in the above ratio of emergent to incident effect for the various metals might be attributed to a selective photo-electric activity on part of the films used. For instance, platinum might respond photo-electrically more easily to shorter wave-lengths than magnesium and hence give a greater value for the ratio of the emergent to the incident effect. At any rate this is a possibility which should be carefully investigated. For this reason the investigation will be continued with the object of determining the value of the above ratios for variations with the wave-length of the incident light.

From the existence of similar effects to those here described, in the case of the  $\gamma$ -rays and Röntgen rays, Bragg has concluded that these radiations are of a corpuscular character.

The results of the present experiments indicate that that part of Bragg's argument applies with equal force to the case of the radiations which produce the photo-electric effect. Since the photo-electric effect can be produced with visible light in the case of sufficiently electro-positive metals, and since there is a continuous gradation between such cases and the effects here investigated, there seems to be no valid reason for supposing that the difference between the emergent and incident effect is not characteristic of both ordinary and ultra-violet light as well as the more penetrating radiations examined by Bragg. If it stood alone this investigation would be a strong argument in favour of the unitary theory of light. The objections to such theories on other and apparently more fundamental grounds are very serious, as Lorentz has recently shown. Under the circumstances it seems desirable to postpone further discussion pending the accumulation of more experimental evidence.

This subject and its method of investigation was suggested by Prof. O. W. Richardson and carried to its present stage under his direction. I wish to thank him here for his valuable assistance, advice, and encouragement throughout the course of this work.

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#### LXXXIV. *A Structural Theory of the Chemical Elements.*

*By* J. W. NICHOLSON, M.A., D.Sc.\*

THIS paper gives a preliminary account of a structural theory of the chemical elements, which derives them as compounds, in a certain sense, of primary forms of matter. It is possible, on certain views, to accomplish this for the simpler elements, and to a greater degree, of course, for those which are more complex, the degree of complexity being measured by the atomic weight.

Calculations of the atomic weights of these hypothetical constructions, even in the simplest cases, can give results in sufficient and indeed unexpected accord with the best chemical determinations. The groupings of primary forms for the elements as arranged in the Periodic Table show curious systems which appear to shed light on the mutual relations of the elements. This is more especially the case

\* Communicated by the Author, having been read at the meeting of the British Association at Portsmouth, 1911.



in the radioactive elements, and it will be seen that a consistent scheme for these transformations can be founded upon the views advocated in the paper—a scheme which readily removes many of the outstanding difficulties. It has not been possible, for reasons of space, to treat these elements at all completely in the paper; but sufficient indications of this point have been given, and the subject will be treated in greater detail later.

Elements which appear out of their places in the Periodic System always appear to need a characteristic construction of a somewhat different type from that of the class of elements with which they are associated, and with which the chemist is unable to find a clear connexion. It may be said that exactly in proportion as a set of elements do form a real chemical class, it has been found possible, as the result of an exhaustive examination, to endow the set with constitutions of a similar nature. Moreover, with elements for which the chemical determination of the atomic weight has been carried out to the second decimal place, it has been possible only in a few cases to find a choice of formulæ which would yield this value equally well.

It is perhaps necessary to point out at once to what extent the paper is speculative. This character must largely belong to it because the subject is treated only from the point of view of atomic weight. But the results are capable of verification in other ways, some of which are indicated. In particular, the actual existence of the primary substances has been verified by a mathematical investigation of their spectra, to be published independently, which shows that they are the origin of the unknown lines in the spectra of the nebulæ and of the solar corona.

The acceptance of these results involves secondary consequences of a far-reaching kind. In the first place, the nature of the positive electricity in the atom is determined, and found to be that supposed by Sir J. J. Thomson in his paper of 1904\*. That is to say, positive electricity is regarded as existing in uniform volume distributions, whose volume is proportional to the positive charge. But in the conception of the structure of a simple atom there is a difference. Sir J. J. Thomson treated the electrons in the atom as revolving inside the positive sphere, which was of atomic size. On the view developed in this paper, positive electricity exists in units very small in radius compared even with the electrons, and is the source of nearly the whole mass of the atom. The revolving system is therefore a planetary

\* *Phil. Mag.* March 1904.

one, and it is noteworthy that Rutherford\*, in a recent paper, has concluded, from the evidence furnished by experiments on scattering, that the planetary system is the most probable. But although the size of the positive units is so different, Thomson's conception of the uniform volume distribution is essential to the calculations of the present theory.

In a complex atom, built up of simpler systems, the assemblage of positive charges is in many respects similar to the assemblage of electrons which revolve round them, and it is not unlikely that many of the positive charges would also revolve. But they are not all of the same size, although the difference in size is not great. Their mass is so great that a disturbance which could expel one of them from an atom would also expel many of the attendant electrons, and it would be impossible to isolate a positive charge. Evidence for the existence of such positive electrons should be furnished by certain experimental results; and this has recently been the case. In particular, a paper by Prof. R. W. Wood† may be mentioned.

The phenomena of radioactivity afford abundant evidence in the same direction. For example, the radium emanation has been shown, by the work of Ramsay and others, to belong without doubt to the argon group of inert gases, and to be a true element for which a vacant space has existed hitherto in the Periodic Table. Yet it gives off the simpler atom of helium. Unless the constituents of this atom already exist as a group, in unstable equilibrium with other groups, in the atom of the emanation, it is difficult to imagine by what means it can be detached as such when a really definite conception of the process is intended. Evidently the difficulty is extreme on Sir J. J. Thomson's view of the atom, which, it must be borne in mind, was only a provisional one adopted mainly for purposes of mathematical simplicity. It is none the less extreme on Rutherford's more recent view, a revival of the suggestion of Nagaoka, of a simple Saturnian system in the atom, involving only a single positive nucleus.

The mode of analysis adopted in this paper has nevertheless, by way of test, been applied to such a system; but it has been found impossible from such a conception to obtain atomic weights in good accord, or in some cases in any accord at all, with chemical determinations for the simpler elements. Similar application has been made to other conceptions of positive electricity—for example, surface distributions of uniform density,—and with the same lack of success. On

\* Phil. Mag. May 1911.

† Phil. Mag. Feb. 1908.

the whole, the investigation has established, with some thoroughness, that the atomic systems dealt with in this paper are, from the point of view of atomic weights, the only type which atoms can have on the basis of a purely electrical theory. We have indicated already some other considerations tending in the same direction.

Another consequence of the adoption of these views is the acceptance of the fact that all inertia is due to electric charges in motion. Much controversy has centred in this question, but, at present, the main trend of opinion is against the existence of any other kind of inertia. Larmor, in his theory of the æther, has adopted this view, and although attempts have been made to explain the results of Kaufmann on rapidly moving electrons by the help of Newtonian inertia, it is found that Bucherer's work gives the most satisfactory theory of these experiments. This work is based on the contraction formula for electrons in motion, and on the supposition that all inertia is of the electrical type. There is no necessity to give further references on this point.

#### *The Primary Substances, or "Protyles."*

The simple elements, from which, or rather from the constituents of which, we propose to construct all the others, consist of single rings of electrons rotating round small nuclei of positive electricity. These nuclei are small compared with the electron, and furnish nearly the whole mass of the atom. The number of these substances whose existence is declared is four; but only three are used in the following constructions. This number is fixed by no other consideration than that more than three are not necessary: as regards the fourth, more will be said later. Moreover, it is remarkable that if the next model simple atoms, in order of mathematical simplicity, are examined, they are found to be quite useless for all the elements of low atomic weight, which constitute the real test, and it is not possible, for example, to obtain the atomic weights of beryllium, boron, and carbon from any compound of protyles involving the next two from those considered in the paper.

The first of these primary substances is an atom containing a single ring of two electrons rotating round a positive nucleus. When this paper was communicated to the British Association, it was suggested that this element would be coronium, the unknown substance (or one of them) present in the solar corona. Subsequent work on its spectrum, which at that time was incomplete, has justified this supposition.

It has been shown by G. A. Schott that a system of rotating electrons would rapidly lose energy unless arranged in rings. From the point of view of the present paper, the actual arrangement does not require consideration; but it is to be noted that the atoms with which we deal can be made to have the necessary permanence by this simple hypothesis. This can be seen intuitively, in fact; for if  $n$  electrons are rotating at equal distances round the same circle, they each have an acceleration of the same amount towards the centre, and the vector sum of these accelerations is zero. This is Larmor's condition for the absence of radiation.

This condition cannot be fulfilled for a single electron; so that the first primary substance must have two, as we have supposed, if an electrically neutral atom of the simplest kind is to be formed.

The second primary substance has three electrons, and a corresponding nucleus of a size, and with a charge therefore, sufficient to make the atom electrically neutral. This has been taken as hydrogen in the paper.

It is important at this point to preclude a misunderstanding; for it is not intended to state that a hydrogen atom contains three electrons. It certainly contains a very small number, whatever its constitution. In order to find a basis for the reckoning of atomic weights, we have subsequently taken such a unit of weight that the protyle with three electrons has a weight 1.008, the atomic weight of hydrogen, and the weights of the other elements are referred to this scale. Compounds are constructed with the weights usually given as atomic; so that the elements, except perhaps hydrogen, all have the correct atomic weights relatively to one another. It remains to secure that they shall be correct relatively to that of hydrogen. If hydrogen is the substance with three electrons, this is secured automatically; but if it is more complex, say equivalent to two atoms of this substance, all the groupings in the subsequent formulæ merely require multiplication by two. We definitely assume that hydrogen is either this substance or a polymer (not quite in the chemical sense), but nothing more definite until further examination has been made. But in order to work out a theory, it is convenient to suppose this substance to be hydrogen, with this reservation.

The third primary substance contains four electrons, with the corresponding positive charge in the nucleus. It is identified, with mathematical justification, as nebulium—the source of the principal lines in the spectra of nebulae.

The fourth substance similarly contains five electrons, and

is provisionally called protofluorine, mainly for lack of a better name. The name has been used before for a hypothetical element with an atomic weight nearly the same. No chemical similarity to fluorine is necessarily denoted. This element appears to be present strongly in the solar corona\*.

The investigations of the spectra of these elements are to be communicated to the Royal Astronomical Society, and will probably be published in part before this paper.

### *The Nature of "Compounds."*

When an element is said subsequently to be a "compound" of simpler elements, the statement does not relate to a compound as ordinarily known to chemists. Something of a more intimate nature is indicated. On the modern view of chemical affinity, valency is believed to be a capacity for taking up or giving off a certain number of electrons, so that when two elements, or ions, have opposite charges, they may be held together in a compound. The "residual" attraction of two molecules may also form an effective compound, as in Sir J. J. Thomson's discussion of the probable nature of chemical action†. But in all truly chemical compounds, the separate atoms of the elements concerned must be supposed to preserve their identity, though held together by chemical forces, that is to say, electrical forces of a particular kind.

This is illustrated from the fact that compound gases have a ratio of specific heats determinable from the number of atoms in the molecule. Now the radium emanation or niton belongs to a group of gases whose other members are monatomic, and this gas is capable of giving off helium—a fact which is difficult to explain if it be monatomic. The difficulty can be evaded by supposing that the atom of the gas contains all the components of the atom of helium, but not as a compound, in any ordinary sense, of the atom of helium with something else. In suitable circumstances, these components are excluded together as a helium atom; but while in the atom of niton they are more intimately related to the major part of the atom. Niton could therefore

\* The strongest lines in the coronal spectrum are due to this substance, and it is therefore perhaps advisable to interchange the names coronium and protofluorine; but in this paper the names used when the paper was read have been retained in order to avoid confusion.

† *Vide* 'The Corpuscular Theory of Matter.'

behave as a monatomic gas, as there is every reason to suppose that it would if the experiment were possible.

Many suggestions could be made as to the probable nature of a compound of this kind. For example, if an element consisted of a compound of nebulium and protofluorine, it might have an atom made up of two coplanar rings of four and five electrons respectively, and two positive nuclei. The essential feature is that these two nuclei should not coalesce into one. The separate elements are there in a sense, but not in the chemical sense, in which the two elements would exist side by side as separate units, held together perhaps by the transfer of an electron from one to the other.

It is needless to dwell at any length upon the question of energy. The knowledge that an immense amount of energy is liberated in radioactive transformations, and that their rate of progress is apparently quite independent of external conditions, such as temperature, which influence ordinary chemical action, is sufficient to indicate the difference between the two types of "compound." When expressions like "compound" and "protyle" are used, it is on account of their convenience, and their limitations of meaning require emphasis.

### *Atomic Weight.*

The weight of an atom, always determined from its inertia, may be regarded as the sum of the inertias of all its positive and negative charges. If the positive charges have a much smaller radius, their inertia will greatly outweigh that of the electrons, and we may neglect the latter for the present. The motions to which a nucleus is subject will always be slow in comparison with the velocity of light. Let  $a$  be its radius, and  $e$  the charge on an electron. If there are  $n$  electrons in a neutral atom of a primary simple substance, the positive charge is  $ne$ , and the inertia will be proportional to  $n^2e^2/a$  by the usual formula for slow motions.

If the positive electricity has a uniform volume density, its volume is proportional to  $ne$ , and therefore  $a$  to  $n^{\frac{1}{3}}$ .

Thus the inertia is proportional to  $n^{\frac{5}{3}}$ . That of a compound atom containing several nuclei associated with rings of electrons will be proportional to

$$\Sigma n^{\frac{5}{3}}.$$

Assuming that the hydrogen atom has three electrons, the

relative weights of the atoms of the primary substances are

$$\text{Coronium} \quad . \quad . \quad n = 2, \quad n^{\frac{5}{3}} = 3.1748,$$

$$\text{Hydrogen} \quad . \quad . \quad n = 3, \quad n^{\frac{5}{3}} = 6.2403,$$

$$\text{Nebulium} \quad . \quad . \quad n = 4, \quad n^{\frac{5}{3}} = 10.079,$$

$$\text{Protofluorine} \quad . \quad . \quad n = 5, \quad n^{\frac{5}{3}} = 14.620.$$

It is usual to take the atomic weight of oxygen as 16; so that hydrogen has an atomic weight 1.008. On this scale, we find:—

$$\text{Atomic weight of Coronium} = .51282,$$

$$,, \quad ,, \quad \text{Hydrogen} = 1.008,$$

$$,, \quad ,, \quad \text{Nebulium} = 1.6281,$$

$$,, \quad ,, \quad \text{Protofluorine} = 2.3615.$$

The atomic weight of coronium is approximately the value assigned by Mendeléef to a hypothetical element. Nebulium may be the element predicted with an atomic weight nearly equal to 2.

### Compound Atoms.

*Helium.*—The terrestrial element succeeding hydrogen is helium, whose atomic weight, as given by the International Committee for the present year, is 3.99.

Again neglecting the weight of the electrons, we find by addition that the weight of an atom consisting of one atom of nebulium and one of protofluorine is 3.9896 or 3.99.

Helium can therefore be expressed as a simple type of compound atom. With the symbols Cn for coronium, Nu for nebulium, and Pf for protofluorine, we may write



where the equation is not to be interpreted in the chemical sense.

Before considering other elements, we must take account of the inertia of the electrons. An estimate of its magnitude may be obtained by the supposition that they are moving slowly. It may be shown by a consideration of the spectral lines that the velocity of the electrons in an atom of nebulium is about .004 C, where C is the velocity of light. The nature of the inertia-formula is such that this can be effectively treated as slow, in the computation of a small effect of this kind.

Now the mass of a slowly-moving electron is  $6.10 \cdot 10^{-28}$  gram, and the mass of a hydrogen atom is  $1.1 \cdot 10^{-24}$  gram, according

to the best estimates. The fraction of the weight of the atom due to its three electrons is therefore practically  $1.67 \cdot 10^{-3}$ , and therefore, if 1.008 be the atomic weight, the weight of the corresponding nucleus is only

$$(1.008)(1 - .00167).$$

The revised weights of the nuclei of the other simple atoms become therefore

$$\text{Cn} = .51196, \quad \text{Nu} = 1.6254, \quad \text{Pf} = 2.3576.$$

Adding the weights of the electrons in each case, on the appropriate scale .00056 for each electron, we have the following results:—

Atomic weight of Coronium	=	.5131,
„ „ Hydrogen	=	1.008,
„ „ Nebulium	=	1.6277,
„ „ Protofluorine	=	2.3604,

the alterations affecting only the third decimal place slightly.

The atomic weight of helium now becomes 3.9881, or again 3.99.

It may be shown that this value persists even if the electrons move so fast as to double their inertia. This would approximately be the case if the velocity of an electron were  $\frac{4}{5}$  of that of light.

We proceed to the consideration of other simple cases before attempting to construct a general scheme. When the helium group enters, it is not implied that this group is always intended rather than its two component groups, which may be differently situated in the atom.

There is a fairly general suspicion that many of the elements may be composed of helium and hydrogen. This view receives some support from the following considerations.

In constructing the elements, coronium is not used. This reduces the number of primary substances to three. The possibility of fortuitous equalities of numbers is thereby greatly reduced. Coronium must be retained as a substance, but it does not seem to have a necessary function in the construction of others, being, like the possible primary substances with six and more electrons, rather a hindrance when the attempt is made to construct the simpler compound elements (with the exception of lithium, a doubtful case) by its combinations with others. It is possible that it is concerned in the composition of the very rare elements, such as



cerium, neodymium, and praseodymium and their group, for these elements occur somewhat strongly in the sun, where coronium undoubtedly exists. If so, some light would be thrown on the apparent lack of places in the Periodic Table for these elements. The atom of coronium would be by no means so permanent as those of other substances, on account of its comparatively rapid radiation.

*Argon.*—The atomic weight of argon has been determined with greater accuracy than those of the other inert gases, and the International Committee now adopts the value 39.88. This is exactly ten times the value we have obtained for helium, and we may write

$$A = 10\text{He}$$

as a provisional representation. The fact that small quantities of argon usually occur in mineral springs which are rich in helium is somewhat suspicious, and when helium is formed in radioactive processes, it is not unlikely that minute quantities of argon should accompany it, if the constituents of the argon atom are the same, in greater number, as in the case of helium. There is some reason to believe that all the inert gases are products of radioactive changes, and the question will be considered in greater detail later.

*Beryllium.*—The combination  $3\text{Pf} + 2\text{H}$  would have an atomic weight 9.097, or 9.10, the International value for beryllium.

*Boron.*—The International atomic weight of boron is 11.00. The combination  $2\text{He} + 3\text{H}$  gives this value exactly.

*Carbon.*—The value of the atomic weight of carbon is 12.00, although the best chemical determinations indicate a value slightly higher. The number 12.008, where the last figure may be smaller, may be obtained from the compound  $2\text{He} + 4\text{H}$ .

*Nitrogen.*— $2\text{He} + 6\text{H}$  gives a value 14.02. Values have been obtained by experiment ranging from 14.05 (Stas) to just below 14.01. At present this is the scheduled value, but it is not regarded as certain.

*Oxygen.*— $3\text{He} + 4\text{H}$  gives 15.996, or 16.00, the value proper to the accepted one for hydrogen.

*Fluorine.*—The atomic weight of fluorine has not been determined recently. It is given as 19.0, the second decimal being small but uncertain. The combination  $3\text{He} + 7\text{H}$  gives 19.020.

*Neon.*—The scheduled atomic weight of neon is 20.2, Watson's recent determination giving 20.21. The combination  $6(\text{PfH})$  gives 20.21, and will be taken subsequently

as representing neon. Apparently the group  $(\text{PtH})_3$  has considerable significance in atomic structure, according to the present theory.

*Sodium.*—The atomic weight of sodium is slightly greater than 23, but not so great as 23.01, according to current chemical opinion. The value 23.008 is given by the group  $4\text{He} + 7\text{H}$ .

*Magnesium.*—This is an element, like beryllium, which cannot be composed from the helium and hydrogen groups. Its atomic weight is 24.32, a value given exactly by  $2\text{H} + 5\text{He} + \text{Pf}$ .

*Lithium.*—We have considered all the known elements with atomic weights less than 25, with the exception of lithium, and the addition of argon. Lithium is the element which has presented the only difficulty, and it is possible that this difficulty is only apparent. Until very recently, the atomic weight of lithium was believed to be greater than 7. A recent determination with carefully prepared material, however, gave 6.94, at present the accepted value. It is not unlikely that the actual value may be even smaller.

The combination  $3\text{Nu} + 2\text{H}$  gives 6.90, and  $\text{He} + 3\text{H}$  gives 7.01, the older value. The first combination gives the best result, and is used later. If it should be the case that the second protyle is not hydrogen, but in a sense half of it, so that all groupings should be doubled, this difficulty is removed on addition of the two groups. At present the question must be left open, but there is some reason to believe that the latter view is correct.

#### THE INERT GASES.

After this preliminary sketch, we may proceed to a detailed theory of a definite group of elements in the Periodic System, and for this purpose we select the inert gases, including the radioactive emanations. They are a very fundamental type of matter, and the groupings which are found to be effective in representing them, from the point of view of atomic weight, have an important place in the suggested constitution of the other classes of elements. Too much stress must not be laid, in many cases, on the particular arrangements selected, which are purely speculative and provisional, but it seems probable that they may represent something in the structure of the atom, from the constant recurrence of those which are effective. It may be claimed that they introduce a system into the Periodic Table which does not appear to be fortuitous, at the same time enlarging

the scope of the table. In the atom, they may be regarded as partially isolated from the rest, though not preserving their identity so completely as in an ordinary chemical compound. A rearrangement typical of radioactive change may be capable of rejecting a group, which may appear as an  $\alpha$  particle. It is possible, as we shall see later, to give a speculative theory of some of the radioactive processes on this basis, which, however crude and incapable of verification in its present form, is certainly not in opposition to any of the phenomena known with certainty. Its capacity for verification is, however, in some respects very real, as will appear. The investigation also serves the purpose of indicating some lines on which valuable experiments might be made.

As an example of this, we may cite the generally accepted view that all  $\alpha$  particles are positively charged atoms of helium. The value of  $e/m$  for these particles is not regarded as certainly accurate, and serves merely to indicate that they are of atomic size. The belief that they are helium rests entirely upon the spectroscopic investigations of Ramsay and others with regard to the products of disintegration of niton or radium emanation, and the more recent work of Rutherford and Royds referring only to a particular case\*. These experiments prove that helium is one of these products, but they certainly do not prove that all the  $\alpha$  particles from the radium or thorium series consist of helium. There is, in fact, strong reason to doubt this view, and it will be sufficient to mention only two facts in this connexion.

In the first place, not only was the helium spectrum obtained in these experiments, but three other lines, of wavelengths 6180, 5695, and 5455 which have never been identified. These results have been confirmed, and certainly seem to indicate a gas other than helium or any known terrestrial substance. The same spectrum is found for the gas liberated by solution of radium bromide.

The excess of hydrogen liberated in experiments with the emanation has also never been explained satisfactorily, and there is some doubt whether it is due entirely to moisture which has found its way into the apparatus. The writer feels compelled to express the belief that some  $\alpha$  particles are not helium, but hydrogen and other substances, more especially nebulium, or more probably  $Nu_2$ , another elementary gas, and it is very desirable that more spectroscopic work

\* A paper by Rutherford and Boltwood (Phil. Mag. October 1911), which has appeared since this was written, gives much more definite proof, but it again does not show that the helium may not be a modified  $\alpha$  particle in many cases.

should be done in all possible cases. It seems not unlikely that some of the lines of the nebular and coronal spectra would be found, just as helium has been found.

Some calculations which may be made from the experimental results are very significant, and one or two may be cited as illustrations. In the first place, though the methods of finding  $e/m$  for the  $\alpha$  rays from radium have been criticized, they have led to very concordant results. Rutherford's original investigation by the electric method gave  $e/m = 6 \cdot 10^3$ . The photographic method of Des Coudres gave a value  $6 \cdot 4 \cdot 10^3$ , and this was confirmed later by Rutherford by a combination of the magnetic deflexion and the heating effect, which gave  $6 \cdot 5 \cdot 10^3$ . This agreement is remarkable, and certainly an indication that the results are probably correct. Now the value of  $e/m$  for a hydrogen atom with the electronic charge, as in electrolysis, is  $9 \cdot 62 \cdot 10^3$ . Taking

$$e/m = 6 \cdot 4 \cdot 10^3$$

for the  $\alpha$  particle, its mass becomes therefore 1.5 times that of the hydrogen atom. If it has a double charge, this becomes 3 times that of the hydrogen atom. This does not point to helium as the  $\alpha$  particle, but to the gas  $Nu_2$ , which we may call Dinebulium, with an atomic weight 3.25. This may be the origin of the three spectral lines already mentioned. There is evidence that the  $\alpha$  particles from the emanation differ either in mass or velocity from those of radium. Rutherford has concluded that they have a smaller velocity. It is possible, however, that they have a larger mass, and really consist of helium.

One more calculation of considerable interest may be given. Becquerel has concluded that the amount of deviation, in a given magnetic field, is the same for the  $\alpha$  rays of polonium and radium. This means that the momentum  $mV$  of the rays is the same. But the  $\alpha$  rays from polonium are much more readily absorbed, and therefore apparently  $m$  is greater for these rays. In Rutherford's treatise\* a comparative table of the absorptions is given. For a single thin layer of aluminium foil, the ratio of decrease is, for polonium, .41, and for radium, .48. Afterwards polonium rays cease to follow the exponential law. In a single thin layer, it cannot be very invalid to suppose the decrease proportional roughly to the velocity, or the time which it would take a ray to get through. If, then, the  $\alpha$  ray from radium is really dinebulium, that from polonium has an atomic

\* 'Radioactivity,' p. 162.

weight  $3.25 \times 48 \div 41$  or  $3.8$ . This is consistent with the theory that the polonium  $\alpha$  rays are actually helium.

This digression has been somewhat long, but it serves a useful purpose. Nebulium and protofluorine, even if not primary substances from which others are built up in this particular way, are not hypothetical, as a consideration of spectra shows.

We may now proceed further with the main argument. Of the inert gases, we have already considered helium, argon, and neon.

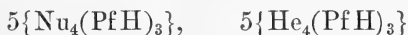
*Krypton and Xenon.*—The inert gases may be divided into the argon and neon groups, if the arrangement in double columns of the Periodic Table be adopted, that is to say, the arrangement which places potassium, rubidium, and caesium in one subgroup, and sodium, copper, silver in another of the same column. In the argon subgroup, the sequence is argon, krypton, xenon, an unknown gas, and niton. The only other member of the parallel group at present known is neon, and it is followed by four vacant spaces. Sir William Ramsay has suggested that the vacant spaces should be occupied by emanations, possibly present in the atmosphere, but decomposed during the process of separation. We shall endeavour to fill these spaces, guided in our selection of formulæ by the groupings of primary atoms found effective for other elements.

We consider krypton and xenon in the first place. Argon has already been classified as  $\text{He}_{10}$ , and neon as  $(\text{PfH})_6$ . It is preferable to write



for the groups  $\text{He}_2$  and  $(\text{PfH})_3$  appear to have some significance.

Consider now the groupings



with an obvious relation to each other and to those of argon and neon. If they represent elements, the calculated atomic weights of these elements are respectively  $83.08$  and  $130.28$ . The present International atomic weights of krypton and xenon are  $82.9$  and  $130.2$ , which, allowing for errors of experiment, especially likely in the case of krypton, are in very close accord with these calculated numbers. Without further discussion, we shall consider these formulæ to represent the atoms of krypton and xenon.

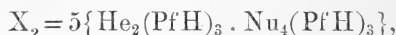
Passing now to the neon group, the first vacancy occurs

just before copper in the Periodic Table, and the hypothetical element has been predicted to have an atomic weight about equal to 63. The formula



which we select, in accordance with necessary selections for other elements, gives an atomic weight 62.88. The unknown gas is called  $X_1$ , and it is possible that the incomplete groupings involving  $\text{He}_2$ ,  $\text{Nu}_2$  are a criterion of instability. The possibility of a decomposition of this gas into the other inert gases with necessary stability is evident from the formula.

Returning to the argon group, we note that the gas preceding niton has a predicted atomic weight of about 176, by the usual method of the Periodic Table. This value has been mentioned, for example, by Sir William Ramsay. Calling it  $X_2$ , we may try a formula



giving the atomic weight 173.5. It contains a possibly unstable group, and may readily decompose into the inert gases of the atmosphere.

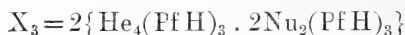
An alternative formula is



with an atomic weight 175. The latter is preferable, but a real decision could only come with a knowledge of the gas. The second formula may illustrate a relation with niton, and it notably combines the double grouping of the neon series and the quintuple one of the argon series, besides giving a better value for the atomic weight.

It is worth the trouble to continue these speculations regarding unknown gases, though briefly, since one of them is generally believed to be the emanation from actinium.

The next vacancy in the neon group immediately precedes silver, and the corresponding gas should have an atomic weight of about 106. We suggest



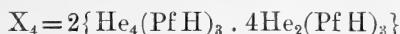
or



with an atomic weight 105.6. These might be different elements, with the same groupings arranged differently. Examples of this are not unknown, and the case of uranium and uranium X may be cited.

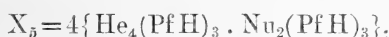
These gases contain, throughout the series, a possibility of disintegration into the gases of the atmosphere.

Another vacancy precedes gold in the Table, the probable atomic weight concerned being 197. We suggest the gas



with an atomic weight 196.76, exhibiting both the double and quintuple groupings of the more primary groups.

We have passed over a vacancy on the horizontal row containing a series of the metals of the rare earths. There is a current view that samarium (150.4), europium (152.0), and gadolinium (157.3) form a triad in the last column of the table, like iron, nickel, and cobalt, or osmium, iridium, and platinum. Terbium (159.2) then appears in the column with copper, silver, and gold, and should be preceded by an inert gas of the neon group with an atomic weight nearly equal to 158. If this view be accepted, the only compound of the usual groupings which is available is, with atomic weight 157.6,



which is not quite in line with the general scheme.

But a consideration of the table appears to indicate that the true value should be nearly 153, if the successive differences are accounted in the usual way. The position of the rare earths is a baffling problem, and there is certainly no resemblance between terbium on the hand, and copper, silver, and gold on the other. In fact, the rare earths all resemble lanthanum, the first member of their series, in properties, and there is considerable justification for the proposal which has been made to extend the row to 16 instead of 8 members at this stage of the table. Quite apart from the present theory, it does not seem that terbium can retain its place, on purely chemical grounds, in the alkali column. We shall suppose, therefore, that 153, the value naturally suggested by the Periodic Table, is the proper approximate atomic weight of the gas now in question. We suggest therefore the formula



with an atomic weight 152.49. There are other important considerations in favour of this formula, which cannot be discussed at present without undue digression. They will be dealt with to some extent later in the paper, and more specially afterwards. We may, however, state that there is

considerable reason for the belief that this gas is the actinium emanation.

*Thorium Emanation.*—If the thorium emanation is derived from thorium by the expulsion of two  $\alpha$  particles, both being helium atoms, the atomic weight of this emanation is about  $224\cdot4$ , or very close to the value for niton. The decimal in the atomic weight of thorium is not definitely settled, but it is evident that the atomic weights of the two emanations are within a few units of each other, and this fact renders it possible to take up a definite position with regard to them.

If the Periodic Table is to be accepted at all, it is evident that it contains no places for two inert gaseous elements so close together. Thorium emanation, though more unstable, is as much an element as niton. The suggestion may be made that the atomic weights of these emanations are *identical*, but that they consist of the same groupings in the atom arranged differently, in a more stable manner in the case of niton. Examples of elements with identical atomic weights are familiar in radioactive transformations. The case must occur whenever one element is derived from another by the expulsion of  $\beta$  particles and  $\gamma$  rays only. Two such emanations could break down in different ways.

This seems to be the only possible solution of the difficulty, and it is a matter which could perhaps be tested by spectroscopic work. For it involves the conclusion that the  $\alpha$  particles from thorium and radium are not of the same character, if thorium is really the active constituent in its preparations.

*Actinium Emanation.*—A probable constitution of this emanation has been suggested, which leads to an atomic weight of  $152\cdot49$ . It is possible to obtain some degree of experimental verification of this value. Of the various attempts which have been made to find this atomic weight, that of Russ\* appears to be the most satisfactory. The method of diffusion was used, and special precautions taken against unusual behaviour of small quantities of gas. Russ also performed experiments confirmatory of the method, and his final conclusion was that the thorium emanation is  $1\cdot42$  times as heavy as that from actinium. The thorium emanation, in any case, has an atomic weight of about  $222$ , and this leads to a value about  $155$  for actinium emanation.

This is sufficiently close to the value we have suggested, and decides the place of the emanation in the table. The atomic weight of actinium itself is therefore about  $160$ . A

\* Phil. Mag., March 1909.



precise value cannot be given until the nature of its  $\alpha$  radiation is established. Without entering into a discussion at this point, the opinion may be expressed that these  $\alpha$  rays consist perhaps of  $\text{Nu}_2$ , with atomic weight 3.25, which could easily be mistaken, except spectroscopically, for helium. There is some reason to believe that this gas may be responsible for the three spectral lines mentioned in an earlier section.

*Radium Emanation or Niton.*—In discussing a probable constitution of niton, we shall suppose that it is derived from radium by the expulsion of an atom of helium. On this point possible doubt has already been expressed, for reasons only partially indicated, though the indications given show that the  $\alpha$  particles from radium and its products cannot all consist of helium. The value of the atomic weight of lead is another indication. The paper of Rutherford and Royds on the collection of the particles in a vessel may prove the matter in this special case. But if we adopt the usual view as a working hypothesis, the atomic weight of the emanation would be 222.4, if the atomic weight of radium is 226.4 as determined by Mme. Curie. The nearest value which can be obtained on the present scheme is given by



with an atomic weight 222.81. It can be arranged in other forms, one of which might be the thorium emanation, and is, in itself, quite consonant with the scheme, preserving the double and quintuple groupings. It still does so if arranged as



Until further evidence concerning the  $\alpha$  particle is available, this formula, in one form or another, will be adopted. If the atomic weight of helium be added, the atomic weight of radium becomes 226.80. This is very close to the value given by Thorpe's experiments, as described in a recent Bakerian Lecture. The formula is well in line with the scheme, but it does not exhibit radium as a transformation product of uranium if only helium is removed in the form of  $\alpha$  particles.

If this value be correct, it reduces the discrepancy between the atomic weight difference of radium and lead, and the weight of the five helium atoms supposed to be ejected in a final transformation from radium to lead. The atomic weight of lead is given as 207.1, and with the value 226.80 for radium, the five  $\alpha$  particles should weigh 19.70, which

is very nearly the value for five helium atoms. The ordinary value for radium gives only 19.3. But this point must not be dwelt upon, as it seems probable that all the particles are not helium, and there may be more than five.

The results of this examination of the inert gases may be collected into the following table, as a representation of the first column of the Periodic Table. The practical value of the atomic weight, when one is generally accepted, is placed in brackets.

## Group I.

Helium, $\text{He} = \text{Nu} + \text{Pf}$ , 3.99 (3.99)	
	Neon, $2(\text{PfH})_3$ , 20.21 (20.2)
Argon, $5\text{He}_2$ , 39.88 (39.88)	
	$\text{X}_1 = 2\{\text{He}_2(\text{PfH})_3 \cdot \text{Nu}_2(\text{PfH})_3\}$ , 62.88
Krypton, $5\{\text{Nu}_4(\text{PfH})_3\}$ , 83.08 (82.9)	
	$\text{X}_3 = 2\{\text{He}_4(\text{PfH})_3 \cdot 2\text{Nu}_2(\text{PfH})_3\}$ , 105.6
Xenon, $5\{\text{He}_4(\text{PfH})_3\}$ , 130.28 (130.2)	
	$\text{Ac Em} = 2\{2\text{He}_2(\text{PfH})_3 \cdot 3\text{Nu}_2(\text{PfH})_3\}$ , 152.49
$\text{X}_2 = 2\{2\text{Nu}_4(\text{PfH})_3 \cdot 3\text{He}_2(\text{PfH})_3\}$ , 175.0	
	$\text{X}_4 = 2\{\text{He}_4(\text{PfH})_3 \cdot 4\text{He}_2(\text{PfH})_3\}$ , 196.76
Niton, $2\{2\text{Nu}_4(\text{PfH})_3 \cdot 3\text{He}_4(\text{PfH})_3\}$ , 222.8	

*Other Groups of Elements.*

After this sketch, necessarily somewhat brief, of the group of inert gases, we may proceed to consider other groups of elements with chemical similarity. Only those of accepted atomic weights are considered, and in particular, all the elements of the rare earths are ignored, since they are uncertain both in atomic weights and positions in the table. It must be stated that in many cases the suggested groupings are entirely provisional, and put forward partly to indicate the possibility of the process. Many considerations, atomic volume for example, would be necessary before anything of a final character could be attempted. But on the whole the system cannot be wholly fortuitous, and the results are suggestive in many ways.

*Lithium, Potassium, Rubidium, Caesium.* — For these elements the following formulæ may be suggested :—

Lithium,  $\text{H}_2\text{Nu}_3 = 6.90$  (6.94),

Potassium,  $2\{\text{Nu}_2(\text{PfH})_3\} \text{H}_2\text{Nu}_2\text{Pf}_3 = 39.08$  (39.1),

Rubidium,  $4\{\text{Nu}_4(\text{PfH})_3\} \text{He}_4\text{H}_3 = 85.44$  (85.45),

Caesium,  $4\{\text{He}_4(\text{PfH})_3\}\{\text{Nu}_4(\text{PfH})_3\} \text{He}_3 = 132.81$  (132.81).

The case of lithium has been discussed already. The formulæ present a definite scheme of development with atomic weight increasing, and their groupings have obvious relations with those of the inert gases. The relations among the metals themselves are of the kind which would be expected on the view that the elements are the representatives of definite positions of stability which have been reached in an evolution of matter from its simplest forms. The properties of these stable systems may be expected to recur at certain intervals, for example, alkaline properties and their chemical associates recur with the groups just written. Other groups of a similar kind might be written down with perhaps similar properties, but capable possibly of only a transitory existence, as in the case of radioactive products. The discovery of radioactivity has already led, as Sir William Ramsay pointed out in his Presidential Address to the British Association at Portsmouth, to the isolation of twenty-seven new "elements," many of which have been shown to possess definite chemical properties. The Periodic Table cannot take account of all unstable as well as stable elements, except on the view that the complete table should contain many times the present number of elements, in which the present set would be but isolated units, and such that the table should find places for whole groups at present unknown, or perhaps represented by a single member, as possibly, for example, in the case of sodium or manganese.

The real existence of a general scheme of this kind is an immediate deduction from the growing belief that all matter is to a certain extent radioactive. Campbell has detected the effect even in potassium, which perhaps gives a series of products for which the present table has no place. Radioactivity can easily be overlooked if the velocity of the expelled particles is below a certain value. It is a process of devolution of matter, and if the  $\alpha$  particle were endowed with considerable mass it could not be detected. A gas like neon may be an  $\alpha$  particle from certain kinds of matter, and it is probable that all the inert gases are waste products of this nature, which have accumulated in the atmosphere.

Their absence from the solar spectrum is significant, and perhaps an indication that in this case the process of devolution has not gone far. If they are radioactive products, the fact that their groups are so effective in the constructions for other elements has an important significance. If an atom of caesium, for example, gave off the group  $\text{He}_3$ , the remainder might disintegrate into krypton and xenon, without any possible detection by experiment.

*Sodium, Copper, Silver, Gold.*—These metals occupy the other sub-group in column 2 of the table, and are not closely related chemically, even in respect to valency. Sodium presents much more similarity to the alkali metals, but is devoid of some of their characteristic properties—it does not, for example, form alums. In the alkali group, lithium itself is somewhat exceptional, especially as regards its spectrum, as Hicks\* has shown recently. The formula ascribed to it is not quite similar to those of the allied metals, as it only contains two of the primary substances.

Similar remarks apply to sodium in the present group. It is chemically unlike copper, silver, and gold, and it has been found impossible to obtain a formula quite in line with those of the other metals, nor conversely, to endow them with formulæ similar to that of sodium. It seems likely that sodium is the only stable representative of a whole group of elements. The formulæ suggested for the present elements are:—

Sodium,  $\{\text{Nu}_2 (\text{PfH})_3\} \text{H}_2 \text{Nu}_2 . \text{PfH}_2 = 23.008 (23.0)$ ,

Copper,  $2\{\text{He}_4 (\text{PfH})_3\} \text{Pf}_2 . (\text{PfH})_2 = 63.57 (63.57)$ ,

Silver,  $4\{\text{Nu}_4 (\text{PfH})_3\} 2\{\text{Nu}_2 (\text{PfH})_3\} \text{He}_2 . (\text{PfH})_2 = 107.89 (107.88)$ ,

Gold,  $8\{\text{He}_2 (\text{PfH})_3\} 2\{\text{He}_2 \text{Nu}_2 (\text{PfH})_3\} \text{Nu}_2 (\text{PfH})_2 = 197.3 (197.2)$ ,

where the formula for sodium has a pronounced similarity to that of potassium in the previous section.

*Beryllium, Calcium, Strontium, Barium, Radium.*—The spectrum of beryllium is abnormal in the same manner as that of lithium, and is not of the same type as those of its associated members of the table. This peculiarity has been pointed out to me by Prof. W. M. Hicks, who has not yet published his investigations of these series. We may expect to find a similar divergence in its formula, and this occurs.

\* Phil. Trans. A. 1909.

The suggested formulæ are :—

Beryllium,  $\text{Pf}_3\text{H}_2$  or  $\text{Pf}(\text{PfH})_2 = 9.10$  (9.1),

Calcium,  $2\{\text{Nu}_2(\text{PfH})_3\}(\text{PfH})_3\text{Nu}_2 = 40.084$  (40.09),

Strontium,  $4\{\text{Nu}_2(\text{PfH})_3\}\{\text{He}_2\text{Nu}_2(\text{PfH})_3\}\text{Nu}_3\text{He}_2 = 87.64$  (87.63),

Barium,  $4\{\text{He}_4(\text{PfH})_3\}\{\text{He}_2(\text{PfH})_3\}\text{Pf}_3\text{He}_2 = 137.37$  (137.37),

Radium,  $8\{\text{He}_2\text{Nu}_2(\text{PfH})_3\}2\{\text{He}_2(\text{PfH})_3\}\text{He}_5 = 226.8$  (226.4).

Beryllium diverges very much in the same way as lithium, containing only two primary substances. It involves  $\text{Pf}_3\text{H}_2$  in place of  $\text{Nu}_3\text{H}_2$ . That it should have a different valency from lithium may be seen. Even to protofluorine and nebulium themselves definite valencies can be ascribed on mathematical principles, but this question lies outside the range of the present preliminary exposition of the theory. The valency of an element will have no immediate relation to the valencies of other and simpler elements which could be formed by an arbitrary selection of some of its groups. Valency is, of course, not an idea which can be attached with any meaning to a group like, for example,  $\text{He}_3$ , unless the arrangement in this group be specified, and unless it be unaccompanied by other groups. Perhaps this remark is necessary to emphasise the distinction between compounds in the present sense and chemical compounds.

The formula for radium is obtained on the supposition that its  $\alpha$  particle is helium.

*Magnesium, Zinc, Cadmium, Mercury.*—These metals occupy the other half of the column containing the calcium group, and possess a certain degree of similarity, especially zinc and cadmium. The suggested formulæ are :—

Magnesium,  $\text{NuHe}_4(\text{PfH})_2 = 24.32$  (24.32),

Zinc,  $2\{\text{He}_4(\text{PfH})_3\}\text{Nu}_4(\text{PfH})_2 = 65.36$  (65.37),

Cadmium,  $4\{\text{He}_2(\text{PfH})_3\}\text{He}_6\text{Pf}_4(\text{PfH})_2 = 112.43$  (112.40),

Mercury,  $8\{\text{He}_2(\text{PfH})_3\}2\{\text{Nu}_2(\text{PfH})_3\}\text{He}_6\text{He}_4(\text{PfH})_2 = 200.1$  (200).

The formula for magnesium is somewhat different from the others, but there is a corresponding chemical difference. Beryllium and magnesium have much in common, and the formula for beryllium may be written as  $\text{Pf}(\text{PfH})_2$ , which is very similar to that of magnesium. The other three formulæ follow the usual line of development, with a corresponding gradation of chemical properties.

*Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth.*—Columns 4 and 5 of the table do not contain many elements whose atomic weights have been determined with sufficient

accuracy. They are accordingly passed over in the present sketch, and we proceed to column 6. In this column elements like vanadium and niobium will not be considered. They are classed with nitrogen, to which they have little resemblance, except perhaps in the formation of salts similar to the nitrates, and of oxychlorides. But phosphorus, arsenic, antimony, and bismuth form a series whose properties change continuously from non-metallic to metallic. Nitrogen is also, in some respects, a starting-point of this series. The suggested formulæ are :—

Nitrogen,  $H_4 \cdot He_2H_2 = 14\cdot02$  (14·01),

Phosphorus,  $\{He_2 (PfH)_3\} He_3H = 31\cdot05$  (31·04),

Arsenic,  $3\{He_2 (PfH)_3\} \{Nu_2 (PfH)_3\} Pf_2NuH = 74\cdot96$  (74·96),

Antimony,  $3\{He_4 (PfH)_3\} 2\{He_2 (PfH)_3\} Nu_3H = 120\cdot22$  (120·2),

Bismuth,  $8\{He_2 (PfH)_3\} 4\{Nu_2 (PfH)_3\} Nu_2 (PfH)_2 = 208\cdot08$  (208).

The formulæ for phosphorus, arsenic, and antimony have much in common, but that for bismuth is more reminiscent of some of the preceding metals, though at the same time not unlike the others of its group. The factor 3 in the inert gas groupings appears for the first time in arsenic and antimony, semi-metallic elements. It appears again in the next group of elements.

*Oxygen, Sulphur, Selenium, Tellurium.*—Of these four elements of column 7 of the table, the last three form a pronounced chemical series. Oxygen has little real relation to the others, and certainly none to chromium, molybdenum, and tungsten, which are its actual companions in the subgroup. It is probable that it ought to have a column of its own. But just in so far as nitrogen is, in some respects, allied to phosphorus, so is oxygen to sulphur. It is very easy, for example, to replace oxygen by sulphur in many classes of organic compounds. The formula might therefore be expected to show some relation to the other three. The following may be suggested :—

Oxygen,  $\{Nu_2 (PfH)_3\} NuH = 16\cdot00$  (16·00),

Sulphur,  $\{He_4 (PfH)_3\} HeH_2 = 32\cdot06$  (32·07),

Selenium,  $3\{Nu_4 (PfH)_3\} 2\{Nu_2 (PfH)_3\} NuH = 79\cdot20$  (79·20),

Tellurium,  $4\{He_2Nu_2 (PfH)_3\} 2\{He_2 (PfH)_3\} HeH_2 = 127\cdot5$  (127·5).

There is a curious similarity between the formulæ for selenium and arsenic, and in fact between the last two sets of formulæ. In each case it is accompanied by a gradual

transition to the metallic state, selenium and tellurium having metallic varieties.

*Fluorine, Chlorine, Bromine, Iodine.*—Chlorine, bromine, and iodine form a well-defined chemical series, but fluorine is in some respects isolated, though quite fairly in accord with the others. But it has many exceptional properties, such as its extraordinary affinity for silicon. These elements are accompanied in the column by manganese, which cannot be regarded as related to them. The following may be suggested :—

Fluorine,  $\text{Nu}(\text{PfH})_3 \cdot \text{H}_2(\text{NuH})_2 = 19.02 (19.0)$ ,

Chlorine,  $2\{\text{Nu}_2(\text{PfH})_3\} \text{H}_2(\text{PfH})_2 = 35.47 (35.46)$ ,

Bromine,  $4\{\text{Nu}_4(\text{PfH})_3\} \text{H}_2\text{Pf}_2(\text{PfH})_2 = 79.93 (79.92)$ ,

Iodine,  $4\{\text{He}_4(\text{PfH})_3\} \text{He}_4(\text{PfH})_2 = 126.92 (126.92)$ .

In the case of fluorine, the atomic weight is not known to the second decimal, so that the alternative

Fluorine,  $\{\text{Nu}_2(\text{PfH})_3\} \text{Pf Nu}_2 = 18.98$ ,

is also worthy of consideration. These are the only two alternatives.

*Chromium, Manganese, Iron, Nickel, Cobalt.*—These metals occupy paradoxical positions in the table. Chromium appears as related to oxygen, and manganese to fluorine, while iron, nickel, and cobalt appear as a triad after the eighth column. It is significant that all appear consecutively in a row. Chromium is further associated, with some chemical correspondence, with molybdenum and tungsten. No analogue of manganese has been discovered, and it is followed only by vacant spaces.

There is a considerable similarity amongst these metals, for example in their capacity for forming salts such as the bichromates, permanganates, and ferrates. Moreover, iron, nickel, and cobalt are the magnetic metals. These considerations point to some factor in their constitution which has not occurred in the groups of elements already discussed, and it is noteworthy that an application of the usual groupings is not very successful. The best representations found are as follows :—

Chromium,  $4\text{He}_2\{\text{He}_2(\text{PfH})_3\} \text{H}_2 = 52.00 (52.00)$ ,

Manganese,  $6\text{He}_2 \cdot \text{Pf}_3 = 54.938 (54.93)$ ,

Iron,  $6\text{He}_2 \cdot \text{He}_2 = 55.84 (55.85)$ ,

Nickel,  $4\text{He}_3\{\text{He}_2(\text{PfH})_3\} \text{HePf}_2 = 58.69 (58.68)$ ,

Cobalt,  $4\text{He}_2\{\text{He}_2(\text{PfH})_3\} \text{HHe}_2 = 58.97 (58.97)$ .

These form a very definite system, with the peculiarity that the usual groupings are replaced to a great extent by helium groups. When the suggested constitution of argon,  $5\text{He}_2$ , is considered, it is seen that they do not violate the usual relation to the inert gases.

Perhaps this preponderance of helium, that is to say, of the positive charges of only two types which may be the nuclei of the helium atom, may be responsible for the peculiar properties and isolated position of these elements. It is especially noteworthy that the formula for iron consists only of these.

*Uranium.*—Perhaps a suggestion with respect to the relation between uranium and actinium may be made at this point, though it is highly speculative. If the present atomic weight of uranium, recently determined carefully, be accepted it is in accordance with the constitution

$$\text{Uranium, } 8\{\text{Nu}_2(\text{PfH})_3\}4\{\text{He}_2\text{Nu}_2(\text{PfH})_3\}2\{\text{He}_2(\text{PfH})_3\}=238.50,$$

giving this accepted value exactly. This formula is a multiple of 3. Actinium is believed to be a branch product of the activity of uranium, and there is certainly a considerable gap between the atomic weights. An instability arising in an atom of uranium may in certain cases cause instability in a neighbouring atom, or the unstable atom may be projected into the stable one, so that they break up together. If this should happen three atoms or more of a new substance may be formed, presuming that the result is not a mixture of elements. If three atoms were formed the atomic weight of the substance would be  $\frac{2}{3}$  of that of uranium, or 159.00. Its constitution might be arranged as



derived directly from the formula for uranium. The escape of two  $\alpha$  particles of constitution  $\text{Nu}_2$  and atomic weight 3.25 would then leave the substance already indicated as the probable actinium emanation. If four  $\alpha$  particles escaped each might be nebulium.

It is noteworthy that in the September number of the Philosophical Magazine Mr. G. N. Antonoff describes experiments which seem to indicate a branch product  $\text{UrY}$  derived in small quantity from uranium. This product appears to give off  $\alpha$  rays, but not to the extent expected from the  $\beta$  radiation. If it be the parent of actinium, perhaps these  $\alpha$  rays are not from  $\text{UrY}$ , but from one of its products.

At this point it is convenient to close the present paper. The views which have been advocated are capable in several



ways of experimental test, more especially in connexion with spectroscopic work of the kind already done by Ramsay, Soddy, Rutherford, and others. They do not appear to be at variance with any established experimental result where comparison is possible, and they may serve to suggest useful directions of experimental inquiry, or the outlines of an interpretation of radioactive changes. It may be noted that, according to these views, the number of electrons in an atom is roughly proportional to the atomic weight. The ratio is generally about 2.5, rather smaller than Crowther's estimate.

LXXXV. *On Electrostriction.* By E. P. ADAMS, *Ph.D.*,  
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THE object of the present paper is the development of formulæ for some important cases of electrostriction, particularly those involving cylindrical condensers. M. P. Sacerdote† found the elongation per unit length of a charged cylindrical condenser to be

$$e = \left( \frac{1}{E} + k_1 \right) \frac{K}{8\pi} \left( \frac{V}{d} \right)^2, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $E$  is Young's modulus,  $K$  the dielectric constant, and  $d$  the small thickness of the dielectric, and  $k_1$  a constant involving the dependence of  $K$  upon the state of stress in the dielectric. This expression was obtained by the energy method; when applied to a finite portion of an infinitely long cylinder there is some doubt as to the validity of this method. In the present paper this and other problems are solved by means of the general equations of equilibrium of elastic solids. An entirely different result is obtained for the elongation of a charged cylindrical condenser, and this has an important bearing upon the interpretation of the experiments of Prof. L. T. More‡, who concluded that the whole elongation he obtained could be accounted for by the heat developed as a result of the high difference of potential it was necessary to employ; this conclusion is supported by the result of the present investigation.

It is well understood now that the system of stresses in dielectric media formulated by Maxwell is only approximate, no account being taken by him of the change in the dielectric

\* Communicated by the Author.

† 'Recherches Théoriques sur les déformations électriques des diélectriques solides isotropes.' Paris, Theses No. 1012, 1899.

‡ Phil. Mag. [5] l. p. 198 (1900); [6] vi. p. 1 (1903); x. p. 676 (1905).

constant resulting from the strains in the dielectric. For a homogeneous uncharged isotropic dielectric the three components of the force acting on unit volume are\*

$$\{F_x, F_y, F_z\} = -\frac{1}{16\pi}(\delta_1 + \delta_2) \left\{ \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right\} R^2, \quad (2)$$

where  $R$  is the resultant electric intensity measured in electrostatic units, and  $\delta_1$  and  $\delta_2$  are two material constants which may be defined as follows:—Let, in the notation of the theory of elasticity †,  $e_{xx}$  .....  $e_{xy}$  be the strain components, and let the  $x$ -axis be taken in the direction of the electric intensity at a given point of the medium. Then

$$\left. \begin{aligned} \frac{\partial K}{\partial e_{xx}} &= \delta_1 & \frac{\partial K}{\partial e_{yy}} &= \frac{\partial K}{\partial e_{zz}} = \delta_2 \\ \frac{\partial K}{\partial e_{yz}} &= \frac{\partial K}{\partial e_{zx}} = \frac{\partial K}{\partial e_{xy}} = \frac{1}{2}(\delta_1 - \delta_2) \end{aligned} \right\}, \quad \dots \quad (3)$$

while the derivatives of  $K$  with respect to the other strain components all vanish for an isotropic medium.

The complete system of stresses in an uncharged homogeneous isotropic dielectric is given by ‡

$$\left. \begin{aligned} P_{xx} &= \frac{K}{8\pi}(X^2 - Y^2 - Z^2) - \frac{1}{8\pi}(X^2\delta_1 + Y^2\delta_2 + Z^2\delta_2) \\ P_{yy} &= \frac{K}{8\pi}(Y^2 - Z^2 - X^2) - \frac{1}{8\pi}(Y^2\delta_1 + Z^2\delta_2 + X^2\delta_2) \\ P_{zz} &= \frac{K}{8\pi}(Z^2 - X^2 - Y^2) - \frac{1}{8\pi}(Z^2\delta_1 + X^2\delta_2 + Y^2\delta_2) \\ P_{yz} &= \frac{K}{4\pi}YZ + \frac{1}{8\pi}(\delta_2 - \delta_1)YZ \\ P_{zx} &= \frac{K}{4\pi}ZX + \frac{1}{8\pi}(\delta_2 - \delta_1)ZX \\ P_{xy} &= \frac{K}{4\pi}XY + \frac{1}{8\pi}(\delta_2 - \delta_1)XY \end{aligned} \right\}, \quad (4)$$

$X, Y, Z$  being the three components of the electric intensity  $R$ .

\* Pockels, *Encyklopädie der mathematischen Wissenschaften*, Band v., Heft 2, p. 350. The units employed in this article are different from those here employed, thus accounting for the factor  $4\pi$  in this and the following equations.

† Cf. Love, 'The Mathematical Theory of Elasticity,' 2nd ed.

‡ Cf. Pockels, *l. c.*

1. *Elongation of a Cylindrical Condenser with Adherent Armatures.*

Let  $a$  be the internal and  $b$  the external radius of the dielectric tube. The equations of elastic equilibrium in cylindrical coordinates are

$$(\lambda + 2\mu) \frac{\partial \Delta}{\partial r} + 2\mu \frac{\partial \varpi}{\partial z} = -F_r,$$

$$(\lambda + 2\mu) \frac{\partial \Delta}{\partial z} - 2\mu \frac{1}{r} \frac{\partial}{\partial r} (r\varpi) = -F_z,$$

$u$  is the radial and  $w$  the axial displacement,  $\Delta$  the cubical dilatation, and  $\varpi$  the  $\theta$ -component of the rotation.

$$\Delta = \frac{1}{r} \frac{\partial}{\partial r} (ru) + \frac{\partial w}{\partial z},$$

$$2\varpi = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial r},$$

$F_r$  and  $F_z$  are the radial and axial components of the force acting on unit volume of the tube. To solve these equations we assume that there is a uniform axial displacement,  $w = ez$ , where  $e$  is a constant, the elongation of unit length of the cylinder, which is to be determined. We assume also that  $u$  is independent of  $z$ , which will be the case only for an infinitely long cylinder, but will be approximately satisfied for a cylinder long compared to its radius when the end effects may be neglected. We thus have

$$\Delta = \frac{1}{r} \frac{\partial}{\partial r} (ru) + e,$$

$$\varpi = 0.$$

If  $V$  is the difference of potential between the coatings,

$$R = \frac{V}{r} \frac{1}{\log b/a} = \frac{S}{r} \cdot \cdot \cdot \cdot \cdot \quad (5)$$

Then by (2)

$$F_r = \frac{1}{8\pi} (\delta_1 + \delta_2) \frac{S^2}{r^3},$$

and the single equation of equilibrium is

$$(\lambda + 2\mu) \frac{\partial}{\partial r} \left\{ \frac{1}{r} \left( \frac{\partial (ru)}{\partial r} \right) \right\} = - \frac{1}{8\pi} \frac{S^2 (\delta_1 + \delta_2)}{r^3},$$

its solution is

$$u = \frac{1}{2} Ar + \frac{B}{r} + \frac{S^2 (\delta_1 + \delta_2)}{16\pi (\lambda + 2\mu)} \frac{\log r}{r}, \cdot \cdot \cdot \quad (6)$$

A and B being integration constants to be determined by the conditions at the two surfaces of discontinuity.

The normal traction over the surface  $r=\text{const.}$  counted positive for a tension is

$$\widehat{rr} = (\lambda + 2\mu) \frac{\partial u}{\partial r} + \lambda \frac{u}{r} + \lambda e. \quad (7)$$

The normal surface traction at a surface separating a conductor from a dielectric is, for a cylindrical surface

$$\bar{F}_r = -\frac{x}{r} \left( \frac{x}{r} P_{xx} + \frac{y}{r} P_{xy} \right) - \frac{y}{r} \left( \frac{x}{r} P_{xy} + \frac{y}{r} P_{yy} \right),$$

where the electric stress components  $P_{xx}$ , &c., are to be evaluated for the dielectric, since in the conductor the electric intensity vanishes. Putting  $X = xR/r$ ,  $Y = yR/r$ , we find by (4)

$$\bar{F}_r = -\frac{S^2}{8\pi r^2} (K - \delta_1). \quad (8)$$

Equating (7) and (8) to each other for  $r=a$  and  $r=b$  in turn, we find

$$2\mu B = \frac{S^2(\delta_1 + \delta_2)}{16\pi} \left\{ 1 - \frac{2\mu}{\lambda + 2\mu} \frac{b^2 \log a - a^2 \log b}{b^2 - a^2} \right\} + \frac{S^2(K - \delta_1)}{8\pi} \quad (9)$$

$$(\lambda + \mu)A = \frac{S^2(\delta_1 + \delta_2)}{8\pi} \frac{\mu}{\lambda + 2\mu} \frac{\log b/a}{b^2 - a^2} - \lambda e. \quad (10)$$

For an open tube the longitudinal traction must vanish. Hence

$$\widehat{zz} = \lambda \frac{\partial}{\partial r} (ru) + (\lambda + 2\mu) e = 0. \quad (11)$$

This gives

$$\lambda A + \frac{S^2(\delta_1 + \delta_2)\lambda}{16\pi r^2(\lambda + 2\mu)} + (\lambda + 2\mu) e = 0.$$

Hence

$$\frac{S^2(\delta_1 + \delta_2)\lambda}{8\pi(\lambda + 2\mu)} \left\{ \frac{\mu}{\lambda + \mu} \frac{\log b/a}{b^2 - a^2} + \frac{1}{2r^2} \right\} + \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu} e = 0.$$

This cannot be satisfied for a tube of finite thickness. If  $d = b - a$  is small we can put  $r = a$ . We thus find, keeping terms of the first power only in  $d/a$ ,

$$e = -\left(\frac{V}{a}\right)^2 \frac{(\delta_1 + \delta_2)\sigma}{8\pi E} \left\{ 1 + \frac{d}{2a} \frac{1}{1 - \sigma} \right\}, \quad (12)$$

in which  $E$ , Young's modulus,  $= \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$  and  $\sigma$ , Poisson's ratio,  $= \frac{\lambda}{2(\lambda + \mu)}$ .

(12) is the final expression for the elongation per unit length of the thin dielectric cylinder when charged to a difference of potential  $V$ . If the dielectric constant does not depend upon the strain, *i. e.* if  $\delta_1 = \delta_2 = 0$ , the elongation vanishes. In order to compare this with Sacerdote's expression (1) we must neglect the second term in brackets in (12) so as to apply the formula to an infinitely thin cylinder, and we must also determine the constant  $k_1$  in terms of  $\delta_1$  and  $\delta_2$ . In Sacerdote's notation, a traction  $T$  perpendicular to the electric intensity causes a change in  $K$

$$\frac{\partial K}{\partial T} = k_1 K,$$

while a traction  $T'$  in the direction of the electric intensity causes a change

$$\frac{\partial K}{\partial T'} = k_2 K.$$

Using (3) and the stress-strain relations of the theory of elasticity, we find

$$\left. \begin{aligned} k_1 &= \frac{1}{KE} (\delta_2 - \sigma \delta_2 - \sigma \delta_1) \\ k_2 &= \frac{1}{KE} (\delta_1 - 2\sigma \delta_2) \end{aligned} \right\}, \dots \dots (13)$$

or

$$\left. \begin{aligned} \delta_1 &= \frac{KE(2\sigma k_1 + k_2 - \sigma k_2)}{1 - \sigma - 2\sigma^2} \\ \delta_2 &= \frac{KE(k_1 + \sigma k_2)}{1 - \sigma - 2\sigma^2} \end{aligned} \right\}. \dots \dots (14)$$

Equation (1) may then be written

$$e = \frac{1}{8\pi E} \left( \frac{V}{d} \right)^2 \left\{ K + \delta_2 - \sigma(\delta_1 + \delta_2) \right\} \dots \dots (15)$$

This is the expression given by Pockels\*, following essentially the argument of Sacerdote. According to this formula, if  $\delta_1 = \delta_2 = 0$  the elongation does not vanish, but reduces to

$$e = \frac{K}{8\pi E} \left( \frac{V}{d} \right)^2 \dots \dots \dots (16)$$

\* *L. c.* p. 566.

In order to obtain (15) by the method used in this paper it is necessary to equate the longitudinal traction expressed by (11) not to zero, as has been done, but to the reversed longitudinal electric stress,  $P_{zz}$ , given by (4), which gives, in this case,

$$(K + \epsilon_2) \frac{S^2}{8\pi r^2}.$$

When this is done the expression (15) for the elongation of an infinitely thin cylinder readily follows, if terms in  $d/a$  are neglected. But this procedure is equivalent to assuming that the stresses of electric origin are held in equilibrium by elastic stresses. Maxwell\* himself expressly warned against this. In the case of a fluid the error in this procedure is self-evident, for the only elastic stresses possible are pressures equal in all directions which cannot hold in equilibrium the system of electric tensions along the lines of force and pressures perpendicular to them.

That the elongation must vanish when there is no dependence of the dielectric constant upon the state of strain may be seen in another way. Apart from the change in the dielectric constant any elongation is due merely to the attraction of the oppositely charged armatures. This attraction is the resultant of the force  $\frac{2\pi s^2}{K}$  acting normally outwards from each unit surface of the conductors,  $s$  being the surface density of the charge. The surface densities on the inside and outside coatings are

$$\frac{KV\left(1 + \frac{d}{2a}\right)}{4\pi d} \quad \text{and} \quad \frac{KV a\left(1 + \frac{d}{2a}\right)}{4\pi b d}$$

respectively, to the same degree of approximation we have been using. Hence there is uniform pressure of amount

$$p_1 = \frac{KV^2\left(1 + \frac{d}{a}\right)}{8\pi d^2}$$

inside the cylinder, and

$$p_0 = \frac{KV^2 a^2\left(1 + \frac{d}{a}\right)}{8\pi b^2 d^2}$$

\* Treatise, vol. i. p. 165. Cf. also Pockels, *l. c.* Art. 2.

outside. The elongation is given by\*

$$e = -\frac{\lambda(p_1 a^2 - p_0 b^2)}{\mu(3\lambda + 2\mu)(b^2 - a^2)} = 0.$$

We thus have the important result that the elongation of a charged cylindrical condenser is due wholly to the changes in the dielectric constant resulting from the strain in the dielectric.

We have no means at present of determining the amount of elongation, expressed by (12), to be expected. The combination  $\delta_2 - \sigma(\delta_1 + \delta_2)$  may be determined from the experiments of Wüllner and Wien† on the change in capacity of cylindrical glass condensers when stretched. The capacity is given by

$$C = \frac{lK}{2 \log b/a},$$

where  $l$  is the length of the coated part. Let  $T$  be the tension applied. The ratio  $b/a$  is unaltered by a simple longitudinal traction, so that the whole change in the capacity is given by

$$\delta C = \frac{1}{2 \log b/a} (K \delta l + l \delta K)$$

$$\delta l = \frac{lT}{E}$$

$$\delta K = \frac{T}{E} (\delta_2 - \sigma \delta_1 - \sigma \delta_2).$$

Hence we get

$$\frac{\delta C}{C} = \frac{T}{EK} (K + \delta_2 - \sigma \delta_1 - \sigma \delta_2). \quad . \quad . \quad (17)$$

The following table gives the average values of  $\delta_2 - \sigma(\delta_1 + \delta_2)$  calculated from the results of their experiments. The first column gives the designation of the glass, the second Young's modulus determined by stretching, and the third the dielectric constant.

\* Love, *l. c.* p. 141.

† *Annalen der Physik*, xi. p. 619 (1903).

TABLE I.

Glass.	E.	K.	$\delta_2 - \sigma(\delta_1 + \delta_2)$ .
3. Ph. R. ....	6.41 10 <sup>11</sup>	7.73	+0.68
N. Th. R.....	6.26	8.60	-0.94
8. Bl. B. II. ....	5.51	6.99	-0.45
7. Bl. R. I. ....	6.83	6.57	-0.67
10. 477 <sup>III</sup> 4. II. ...	7.015	6.61	-2.54
12. D. F. R. II. ...	5.12	7.22	-2.57
16. L. F. R. II. ...	5.74	7.07	-2.85

$$\sigma = 0.2.$$

The glass which Prof. More used in his experiments was apparently more like one of the first two in this table than any of the others. So that while  $\delta_1 + \delta_2$  cannot be determined, it is very probable that it is much smaller than K, and therefore the elongation of a charged open cylindrical condenser given by (12) will be much less than that given by (16), the expression which Prof. More attempted to verify.

## 2. *Cylindrical Condenser with Non-Adherent Armatures.*

Some of Prof. More's experiments were made with cylindrical condensers, the armatures being separated from the dielectric tube by an insulating liquid. Let K, as before, be the dielectric constant of the solid tube, and K' that of the liquid. For a fluid  $\delta_1 = \delta_2$ . Let  $\delta_3$  be the common value of these two constants for the liquid. Let  $f$  and  $g$  be the internal and external radii of the liquid,  $a$  and  $b$ , as before, those of the solid tube. The electric intensity in the solid is now

$$R = \frac{K'V}{K' \log \frac{b}{a} + K \log \frac{ag}{bf}} \times \frac{1}{r} = \frac{S}{r},$$

and in the liquid

$$R' = \frac{KV}{K' \log \frac{b}{a} + K \log \frac{ag}{bf}} \times \frac{1}{r} = \frac{S'}{r}.$$



By means of (4) we find the normal traction at a surface separating two dielectrics to be

$$F_r = -\frac{(K - \delta_1)S^2}{8\pi r^2} + \frac{(K' - \delta_3)S'^2}{8\pi r^2}.$$

The surface conditions then give

$$2\mu B = \frac{S^2(\delta_1 + \delta_2)}{16\pi(\lambda + 2\mu)} \left\{ \lambda + 3\mu - 2\mu \log a \right\} + \frac{(K - \delta_1)S^2}{8\pi} - \frac{(K' - \delta_3)S'^2}{8\pi},$$

$$(\lambda + \mu)A = \frac{S^2(\delta_1 + \delta_2)\mu}{16\pi a^2(\lambda + 2\mu)} - \lambda e,$$

and the condition that there be no longitudinal traction gives

$$e = -\frac{S^2(\delta_1 + \delta_2)\sigma}{8\pi a^2 E}.$$

It has been assumed that the solid tube is so thin that terms in  $d/a$  may be neglected,  $d$  being, as before, the thickness of the solid tube. Substituting the value of  $S$  already given

$$e = -\frac{V^2 K'^2 (\delta_1 + \delta_2) \sigma}{8\pi a^2 E \left\{ (K' - K) \frac{d}{a} + K \log g/f \right\}^2} \quad (18)$$

If, as in Prof. More's experiments,  $K = K'$

$$e = \frac{V^2 (\delta_1 + \delta_2) \sigma}{8\pi E a^2 (\log g/f)^2} \quad (19)$$

### 3. Increase in Internal Volume of a Charged Spherical Condenser.

The solution of this problem differs from that of the cylinder in that it may be obtained exactly. For an infinitely thin spherical shell Pockels\* gives the solution obtained by means of the general equations of equilibrium of an elastic solid. For the following it will be useful to have an expression carried to one degree higher of approximation, keeping terms of the first power in  $d/a$ . The

\* *L. c.* Art. 5.

solution is found to be

$$u_a = \left(\frac{V}{d}\right)^2 \frac{a}{8\pi E} \left\{ K + \delta_2 - \sigma(\delta_1 + \delta_2) + \frac{d}{a}(1 + \sigma) \left( K + \frac{\delta_2 - \delta_1}{2} \right) \right\}, \quad \dots (20)$$

where  $u_a$  is the displacement of the internal radius,  $a$ , of the shell. The solution of the same problem obtained by Sacerdote by the energy method agrees with this when the proper changes in notation are made. Thus in the case of a condenser formed of closed surfaces no objection can be found to the use of the energy method. The increase in internal volume is given by

$$\frac{dv}{v} = \frac{3u_a}{a}.$$

If there is no dependence of  $K$  upon the strain so that  $\delta_1 = \delta_2 = 0$ ,

$$u_a = \left(\frac{V}{d}\right)^2 \frac{Ka}{8\pi E} \left\{ 1 + (1 + \sigma) \frac{d}{a} \right\}. \quad \dots (21)$$

It is interesting to show that the same result follows by considering the attraction of the oppositely charged conductors, as was done in the case of the cylindrical condenser. There are uniform pressures,  $p_1 = KV^2 b^2 / 8\pi a^2 d^2$  inside and  $p_0 = KV^2 a^2 / 8\pi b^2 d^2$  outside. In this case we have\*

$$u_a = \frac{1}{3\lambda + 2\mu} \frac{p_1 a^3 - p_0 b^3}{b^3 - a^3} a + \frac{1}{4\mu} \frac{a^3 b^3 (p_1 - p_0)}{b^3 - a^3} \frac{1}{a^2}.$$

Substituting the values of  $p_1$  and  $p_0$  just given we get, after some reductions, (21).

#### 4. *Wüllner and Wien's Experiments.*

Wüllner and Wien† measured the increase in internal volume of a cylindrical condenser whose ends were closed by hemispherical condensers of the same internal radius and thickness of dielectric. There is some uncertainty as to the conditions that must be satisfied at the junctions of the condensers; the simplest condition, which also appears to be the most natural one, is that the form of the tube shall remain unchanged on charging. This requires that the displacement of the internal radius of the cylindrical part shall be equal to the corresponding displacement of the spherical part. The former is found to be, by means of (6), (9),

\* Love, *l. c.* p. 139.

† *Annalen der Physik*, ix. p. 1217 (1902).

(10), (5),

$$u_a = \left(\frac{V}{d}\right)^2 \frac{\alpha(1+\sigma)}{8\pi E} \left\{ K + \delta_2 - \sigma(\delta_1 + \delta_2) + \frac{d}{a} \left( K + \frac{\delta_2 - \delta_1}{2} \right) \right\} - \sigma e a.$$

Equating this to (17) we find

$$e = \left(\frac{V}{d}\right)^2 \frac{1}{8\pi E} \left\{ K + \delta_2 - \sigma(\delta_1 + \delta_2) \right\}.$$

It is interesting to note that this is the expression found by the energy method for the elongation of an infinitely thin cylindrical condenser open at the ends (*cf.* eq. 15). The whole increase in internal volume of Wüllner and Wien's tubes is now given by

$$\delta v = 2\pi a(l + 2a)u_a + \pi a^2 l e,$$

or

$$\delta v = \left(\frac{V}{d}\right)^2 \frac{a^2}{8E} \left\{ [K + \delta_2 - \sigma(\delta_1 + \delta_2)](3l + 4a) + \frac{2d}{a}(1 + \sigma) \left[ K + \frac{\delta_2 - \delta_1}{2} \right](l + 2a) \right\}. \quad (22)$$

Putting in this  $\delta_1 = \delta_2 = 0$  we get an expression which differs from the one obtained by Wüllner and Wien only in the small term involving the ratio  $d/a$ . The reason for the difference lies in the fact that the condition at the junction assumed by them is such as to distort the shape of the tube.

Inasmuch as  $\delta_1$  and  $\delta_2$  enter into (22) in a different combination from that in (17) it might seem that the electrostriction experiments of Wüllner and Wien, combined with their experiments on the change in capacity by stretching, would enable  $\delta_1$  and  $\delta_2$  to be determined separately. But the term in (22) involving  $\delta_1$  and  $\delta_2$  in a different combination from that in (17) is multiplied by the small factor  $d/a$ , and the experiments are not certain enough to justify any conclusions drawn from such a calculation. It is of interest to neglect the term in  $d/a$  in (22) and calculate the values of  $\delta_2 - \sigma(\delta_1 + \delta_2)$  from the electrostriction experiments on closed glass tubes. The following table (p. 900) has been prepared in this way, giving this expression for the same kinds of glass tubes as were used in the capacity determinations.

The agreement is seen to be fairly good for the three last

TABLE II.

Glass.	$\delta_2 - \sigma(\delta_1 + \delta_2)$ .
3. Ph. R. ....	-1.35
8. Bl. R. II. ....	-2.89
7. Bl. R. I. ....	-2.10
10. 477 <sup>III</sup> R. II. ....	-2.47
12. D. F. R. II. ....	-3.78
16. L. F. R. II. ....	-3.56

kinds of glass; for the others, the changes in capacity, and hence the quantity  $\delta_2 - \sigma(\delta_1 + \delta_2)$  is so small that very small experimental errors would have a large effect in the determination of it.

LXXXVI. *The Effect of Magnetic Fields on Metallic Resistance.* By C. W. HEAPS\*.

[Plate XVI.]

NUMEROUS investigations have been made on the change of resistance which different metals undergo when they are placed in a magnetic field. Some experimenters have taken up the case where the magnetic field is applied parallel to the direction of the current in the metal, and others have studied the effect when the field is perpendicular to the current. This latter transverse effect has been most completely worked out for different metals by Grunmach †. The longitudinal effect is not so thoroughly understood, because it is more difficult to use a large magnetic field in this case, and hence the change of resistance to be measured is very small. Williams ‡, using a solenoid, has studied nickel and iron for small longitudinal magnetic fields. Barlow §, Patterson ||, and Owen ¶ have employed an electromagnet and so obtained results for large magnetizing forces; but the uncertainty or incompleteness of these results makes a

\* Communicated by Prof. E. P. Adams.

† *Annalen der Physik*, xxii. p. 141 (1907).

‡ *Phil. Mag.* vi. p. 693 (1903); ix. p. 77 (1905).

§ *Roy. Soc. Proc.* lxxi. p. 30 (1902).

|| *Phil. Mag.* iii. p. 643 (1902).

¶ *Phil. Mag.* xxi. p. 122 (1911).

further study of this side of the problem seem well worth while. Then, too, only the strongly magnetic metals have been carefully examined in longitudinal fields; little is known of the behaviour of the para- and diamagnetic metals. The experiments to be described were undertaken with the idea of making a comparative study of the longitudinal and transverse effects in strong and weak fields, and for some other metals besides the ferromagnetic ones.

The apparatus used for measuring the resistances and changes of resistance was essentially a Wheatstone's bridge. Coils of constantan wire, each of 3 ohms resistance, made up three arms of the bridge; in the fourth was inserted the metallic conductor to be examined. The coils were fixed to a hard rubber base and immersed in oil to maintain constant temperature. Variable resistances were arranged as shunts around one arm, and by changing one of these resistances by a fairly large amount balance could be secured when the conductivity of the metallic specimen changed only very slightly. When the effect was too small for this method, deflexions of the galvanometer were observed, and change of resistance computed by calibrating the galvanometer.

The galvanometer was of the four-coil astatic needle type, provided with a triple shield of soft iron, so that the strongest outside field produced no appreciable effect. It was connected up to have a resistance of 3 ohms, and could be made sensitive to  $5 \times 10^{-10}$  ampere.

For producing the magnetic field either an electromagnet or a solenoid could be used. The solenoid was 1 metre in length, had 33 turns per centimetre, and could produce fields as large as 2200 c.g.s. units. It was constructed around a brass tube, inside of which a smaller tube was fixed. The space between the two tubes was kept full of cold running water, and the metal under examination was contained inside the inner brass tube. This inner tube could be filled with oil, so that the heating effects of the solenoid current were reduced to a minimum.

The electromagnet produced fields as large as 10,000 when the pole-pieces were about 4 centimetres in diameter and 2 centimetres apart. This was the distance used in most cases. The pole-pieces were fitted through apertures in opposite sides of a brass box, and this box was filled with water or oil, so that when the metal to be examined was placed between the poles it was immersed in the liquid. Stirrers driven by a fan-motor could be used to keep the liquid in motion, so that little trouble arose in this case from temperature variation of the metal specimen.

The metals to be examined were arranged in different forms, depending upon the field desired and the character of the metal. Iron, nickel, and cadmium were drawn out into fine wire, and for the strong fields of the electromagnet were stuck with shellac in a zigzag fashion upon one side of a strip of mica about 2 cm. square. This thin strip could then be mounted on a brass plate, placed between the poles of the electromagnet, and arranged to turn so that the direction of the current in the zigzag wires could make any desired angle with the magnetic field.

For the small fields of the solenoid the same specimen could be used without modification in measuring the effect of a transverse field. It was simply mounted on the end of a circular hard rubber block and lowered into the solenoid. For longitudinal magnetization in these small fields the wires were supported in a framework consisting of two circular hard-rubber blocks—the blocks just fitting the inner tube of the solenoid—held apart by three brass rods. The wires were connected in series by soldering short copper wires of negligible resistance across the ends. In cases where sagging of the wires occurred the solenoid was set up vertically and weights arranged so that the wires were kept taut.

Manipulation of the Heusler alloy was much more difficult, owing to the extreme hardness and brittleness of this substance. The alloy was obtained from Kahlbaum, and came cast in the form of blocks. A thin section was cut from a block with a diamond saw and cemented to a glass plate. After being ground thin, narrow strips were cut from the section by the use of a small file, and these strips were mounted on mica or glass in the desired position and soldered in series, after having their ends plated with copper. The total resistance thus secured was rather small, as it was not advisable to use very many strips; but the magnitude of the effect was so great that no trouble arose from this source.

The difficulties of the experiments arose chiefly from the smallness of the effects to be measured. In spite of all precautions temperature changes affected the metals to a certain extent. Usually after balance was secured the galvanometer showed a slow and steady drift to the right or left, depending upon whether the metal was growing colder or warmer. By regulating the flow of water between the tubes of the solenoid it was possible to check this drift, or at least the galvanometer could be kept slowly vibrating between two limits. Then by making observations each time the galvanometer came to the same limit the effect of temperature changes was practically eliminated.

It was impossible to get purely longitudinal fields in the electromagnet. With the pole-pieces necessarily so far apart it was inevitable that the field should be non-uniform. In addition, the method of arranging specimens introduced a small transverse component where the wires bent in a zigzag fashion were doubled back upon themselves. This effect was reduced to a minimum by using fine wire and few turns. Its magnitude could be very closely estimated by comparing with the results obtained in the smaller uniform fields of the solenoid for the same metal mounted more perfectly.

In taking readings, the resistance was first measured without the magnetic field, again when the field acted on the metal, and finally another reading was taken without the field. In all cases the magnetizing current was left on for as short a time as possible so as to prevent heating effects. The magnetic field of the electromagnet was measured with a bismuth spiral.

The data secured can best be examined when  $dR/R$ , the change of resistance divided by the resistance in zero field, is plotted against  $H$ , the magnetic force.

#### PLATE XVI.

##### Fig. 1. Iron.

- I. Longitudinal field, using solenoid. Temp.  $23^{\circ}$ .  
Soft Norway iron wire, diam. 0.032 cm. Resistance 2.89 ohms.
- II. Longitudinal field, using solenoid. Temp.  $23^{\circ}.5$ .  
Piano wire, diam. 0.025 cm. Resistance 3.86 ohms.

##### Fig. 2. Iron.

- III. Longitudinal field, using electromagnet. Temp.  $23^{\circ}$ .  
Soft Norway iron wire, diam. 0.017 cm. Resistance 3.53 ohms.
- IV. Angle of  $45^{\circ}$  between current and field, using electromagnet. Same specimen as in III.

##### Fig. 3. Iron.

- V. Transverse field, using electromagnet. Same specimen as III.

##### Fig. 4. Nickel.

- I. Longitudinal field, using solenoid. Temp.  $23^{\circ}$ .  
Diam. 0.050 cm. Resistance 1.25 ohms.

##### Fig. 5. Nickel.

- II. Longitudinal field, electromagnet. Temp.  $23^{\circ}.5$ .  
Diam. 0.017 cm. Resistance 2.75 ohms.
- III. Angle of  $45^{\circ}$  between current and field, using electromagnet. Same specimen as II.

Fig. 6. Nickel.

IV. Transverse field, electromagnet. Same specimen as II.

Fig. 7. Cadmium.

I. Longitudinal field, solenoid. Temp.  $17^{\circ}$ .

Wire, diam. 0.034 cm. Resistance 1.72 ohms.

II. Transverse field, solenoid. Temp.  $17^{\circ}$ .

Strips. Resistance 1.31 ohms.

Fig. 8. Cadmium.

III. Longitudinal field, electromagnet. Temp.  $23^{\circ}$ .

Wire, diam. 0.014 cm. Resistance 1.84 ohms.

IV. Transverse field, electromagnet. Same specimen as III.

Fig. 9. Heusler alloy.

I. Longitudinal field, solenoid. Temp.  $21^{\circ}.7$ . Resistance 0.68 ohm.

Fig. 10. Heusler alloy.

II. Transverse field, solenoid. Temp.  $21^{\circ}.2$ . Same specimen as I., differently mounted.

Fig. 11. Heusler alloy.

III. Longitudinal field, electromagnet. Temp.  $23^{\circ}$ .

Resistance 0.68 ohm.

IV. Transverse field, electromagnet. Temp.  $22^{\circ}.4$ . Same specimen as III.

In addition to the results as plotted, the transverse effect for the Heusler alloy was measured for different fields up to 30,000, and curve IV. was found to remain a straight line up to that point. Also, as the alloy was mounted in the form of rather large flat bars, it seemed possible that the magnetic field might be affected by the form of these bars. To test this a specimen was made up from iron in exactly the same manner and a set of measurements made, but the curve obtained did not differ appreciably from III. for iron.

As curve II. for cadmium was obtained with the metal in the form of flat strips and curve I. with wires, a new set of observations of both transverse and longitudinal effects was made for a given field in the solenoid, using the metal in the form of wire in each case. The means of a large number of trials gave  $dR/R = 4.65 \times 10^{-6}$  for a longitudinal field of 1400, and for the transverse field of the same strength  $dR/R$  was found to be  $5.42 \times 10^{-6}$ . This result is more trustworthy than the results shown in curves III. and IV. in larger fields, because in the solenoid the field is uniform over all parts of the specimen.

It is very evident by comparing curves I. and III. for iron and I. and II. for nickel that a certain error is introduced wherever the electromagnet is used, because of the non-uniform field. The pole-pieces were so far apart that the bending of the lines of force introduced a small transverse component ;



and this, coupled with the transverse field where the wire was bent back upon itself, undoubtedly lowers the maximum and causes the slight drop in the curves. Curves IV. for iron and III. for nickel show the effect of increasing this transverse component.

On the other hand, if the pole-pieces are set closer together the lengths of the metal wires used must be correspondingly decreased, and errors due to inaccurate setting are increased. E. A. Owen\* used wires about 1 millimetre long, and obtained curves for nickel and iron in large magnetic fields. For nickel he found the change of resistance reaching a maximum at a field of 2800, and then decreasing steadily to a minimum. For iron the maximum came at 1900; the curve then turned downward and became a straight line, so that  $dR/R$  diminished as much as  $18 \times 10^{-4}$  from a field of 1900 to one of 30,000. Clearly, Owen's results do not agree with the curves obtained above for longer wires; they are even inconsistent with the more accurate measurements obtained when the solenoid was used. Curve I. for iron continues horizontal after passing Owen's maximum at 1900, and curve I. for nickel shows no signs of a downward tendency at 2200. The slight drop of III. (iron) and II. (nickel) is much less pronounced than the slope of Owen's curves; and furthermore, this drop is a very evident result of a transverse component. It seems probable that with very short wires the field may be affected by polarity of the metal; and this, combined with the difficulty of setting such short wires parallel to the field, will undoubtedly explain Owen's results.

The conclusions arrived at may be stated as follows:—

The increase of resistance of iron and nickel in longitudinal magnetic fields approaches a maximum, but does not grow less after reaching the maximum. For transverse magnetization of these metals there is, as found by Grunmach, first an increase and then a decrease of resistance as the magnetic field increases.

For cadmium the increase of resistance in both longitudinal and transverse fields is, as demanded by Drude's theory, approximately proportional to the square of the field strength. The transverse effect is the larger.

For the Heusler alloy there is decrease in resistance in both longitudinal and transverse fields; and for large fields the change is proportional to the field strength. In the case of longitudinal magnetization, however, the effect may approach a maximum, as measurements could not be made in larger

\* *Phil. Mag.* xxi. p. 122 (1911).

fields than 10,000. The behaviour of the Heusler alloy is of special interest, being so much unlike that of the other metals, and with the exception of the Kerr effect, this is the only respect in which its magnetic properties are markedly different from those of iron.

Application of these results to the electron theory of metallic conduction is rather unsatisfactory. On this theory E. P. Adams\* has derived an expression for the change of resistance of a metal in a transverse field,

$$\frac{dR}{R} = \frac{\delta T}{T} - \frac{1}{4} \frac{e^2}{m^2} H^2 T^2.$$

Here  $R$  is the resistance,  $T$  the free period of an electron, and  $\delta T$  the change in the free period due to the molecular rearrangement produced by the magnetic field  $H$ . This equation satisfactorily explains results. For a longitudinal field a similar expression can be derived. Here the electron pursues a spiral course about the lines of magnetic induction, so that there is an increase of resistance resulting from the changed motion. Corresponding to any change in the free period of an electron the expression for the change of resistance may be derived in the form

$$\frac{dR}{R} = \frac{\delta T}{T}.$$

Here  $\delta T$  is of somewhat broader significance than in the preceding formula. It includes the change of free period due to the altered path of the electron as well as the change due to modified molecular structure. A longitudinal field should thus produce a greater effect than a transverse field; and this is contrary to observed facts. By assuming that the molecular rearrangement due to a transverse magnetic field produces a greater increase of free period than that due to a longitudinal field, the two equations above can be taken as expressing experimental results. However, the effect of magnetization on the molecular structure of a metal is of so complex a nature and is so little understood that the equations probably tell only a small part of the story.

The experimental work was suggested by Professor E. P. Adams, and his advice has been of the greatest help throughout the experiments.

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\* Phys. Rev. xxiv. p. 428 (1907).

LXXXVII. *On the Emission of Electrons by Metals under the Influence of Alpha Rays.* By H. A. BUMSTEAD \*.

IT was observed by Bragg and Kleeman † that when a thin sheet of a metal, such as gold, was interposed in the path of a pencil of  $\alpha$ -rays, the diminution in range produced was less when the metal sheet was far from the source of rays than when it was near ; in other words, the rays seemed to be "stopped" less by the metal when they were going slowly than when they were moving with greater speed. T. S. Taylor ‡ made a careful study of the phenomenon and found that this differential effect increased regularly with the atomic weight of the metal. Substances whose atomic weight was much greater than that of air showed the effect very markedly ; substances, such as paper, whose average atomic weight was nearly equal to that of air did not show the effect at all ; and when a layer of hydrogen was used instead of a solid obstacle, the effect was reversed. By plotting the ionization curves of the  $\alpha$ -rays in air and in hydrogen, Taylor showed that there was exactly the same relation between the ionization in the two gases at different parts of the range as between their relative stopping powers. Where the ionization in hydrogen was greater than in air, the hydrogen was more effective in retarding the rays, and *vice versa* ; and the numerical ratios for the two effects were equal. These results led naturally to the hypothesis that the energy lost by the  $\alpha$ -particles in their progress through a gas was mainly, if not wholly, consumed in the production of ions, and that where the ionization was great (as at the "knee" of the Bragg curve) the  $\alpha$ -particles lost energy more rapidly than where the ionization was less. As the knee is more conspicuous in hydrogen than in air the relative stopping effects of these two gases are easily accounted for on this hypothesis.

Shortly afterward, Geiger § published the results of a repetition of Rutherford's measurements of the velocities of the  $\alpha$ -particle at different points in its range. The measurements were made under more favourable conditions than were possible at the time of Rutherford's original experiments, and Geiger was able to show that the loss of energy by the particles in passing through a layer of air was at least

\* Communicated by the Author.

† Phil. Mag. x. p. 318 (1905).

‡ Amer. Journ. Sci. xxviii. p. 357 (1909) ; Phil. Mag. xviii. p. 604 (1909).

§ Proc. Roy. Soc. lxxxiii. p. 505 (1910).

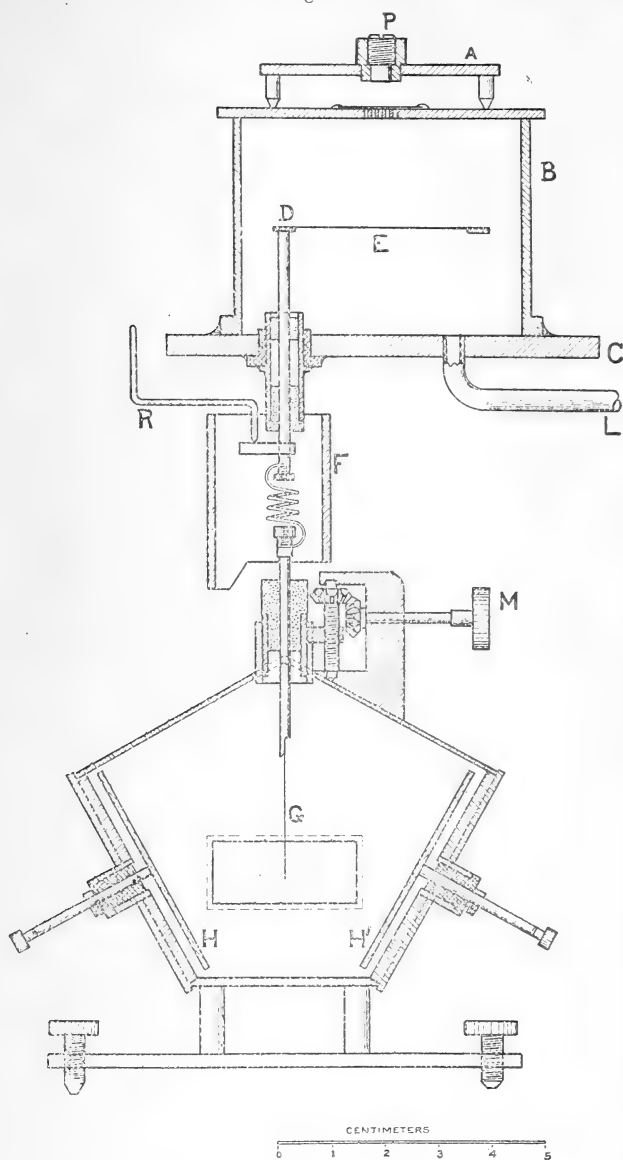
approximately proportional to the ionization produced in that layer, and was not the same for equal paths in air at different parts of the range as Rutherford had supposed. The large value of the ionization as the  $\alpha$ -particle approaches the end of its range involves a correspondingly rapid diminution of its energy, and this rapid expenditure of energy in all probability brings the  $\alpha$ -particle to rest at the end of its range instead of leaving it with a residual velocity after it ceases to ionize, as Rutherford at first supposed.

The continuity of the effects observed by Taylor with hydrogen, air, and various metals of increasing atomic weight made it probable that, in solids as well as gases, the  $\alpha$ -particles expend their energy in a process analogous to gaseous ionization, and that this process follows a curve similar to the ionization curve in gases. Just as the curve for air has a less conspicuous knee than the hydrogen curve, so, from the stopping effects, we should expect the "ionization curve" of gold, for example, to show less projection than the air-curve. According to this view all atoms are less effective in retarding swift  $\alpha$ -rays than slow ones; but heavy atoms are relatively more effective in stopping the swift rays than the light atoms, while they are on more nearly equal terms in their effect upon the slower rays. This view accounts satisfactorily for the results obtained by Taylor.

The following experiments were undertaken to obtain, if possible, some direct evidence of the existence of an ionization process in metals subjected to  $\alpha$ -rays, and to see whether it varied with the speed of the rays in a manner analogous to the ionization which the rays produce in gases. It has been known for some years that a source of  $\alpha$ -rays, or any solid struck by them, emits slow-moving electrons (called  $\delta$ -rays by Sir J. J. Thomson who discovered them). If the atoms of solids are ionized by the  $\alpha$ -rays one would expect that some of the electrons set free in the process from the atoms near the surface would escape from the metal, and that the number escaping would be more or less nearly proportional to the number of atoms ionized. Accordingly, measurements were made of the number of electrons escaping from a thin metal foil when struck by  $\alpha$ -rays at different points in the range.

In order to avoid possible complications from the effects of  $\beta$ - and  $\gamma$ -rays, polonium was used as the source of  $\alpha$ -rays. Professor Boltwood kindly separated the polonium from a solution of radio-lead and it was deposited on the end of a copper plug, 4 mm. in diameter. The first preparation was not very strong and it was necessary to use a system of small

Fig. 1.



capacity in making the electrical measurements. The following form of apparatus was used (fig. 1).

A piece of thin aluminium leaf  $E$ ,  $.064 \times 10^{-4}$  cm. thick, is stretched over the flat brass ring  $D$ , which has

a clear opening of 3.2 cm. The brass rod which supports the ring passes through the base-plate C, and is insulated from it by amber, ebonite, and an earthed guard-tube; the joints are made air-tight with sealing-wax. A cylindrical cover B rests on the base-plate, the two surfaces in contact being ground to each other and made tight with rubber stop-cock grease. The interior is connected by means of the tube L with pump, gauge, and charcoal-bulb. The copper plug P, which has the polonium on its lower end, is supported by a little tripod, and there are punch marks in the top of the cover into which the feet of the tripod fit, so that it can be removed and replaced in the same position. The distance from the polonium to the top of the cover is 6 mm. In the cover, just below the polonium, are nine holes, 1 mm. in diameter, to permit the passage of the  $\alpha$ -rays; these holes are covered by aluminium foil,  $8.65 \times 10^{-4}$  cm. thick. This foil was some that was supplied with tubes intended to demonstrate Lenard rays; it was the thinnest I could find which was not full of holes, and its effect on the range of the  $\alpha$ -particles was equivalent to that of 1.47 cm. of air. It was fastened down to the top with a ring of low melting sealing-wax, which was then covered with stopcock grease.

The rod which supports the ring and aluminium foil was connected to the gold leaf of an electroscope which had been made some time before in this laboratory. It may be regarded as developed from a Wilson tilted electroscope in the same manner that a twinned crystal is developed from an ordinary one. The two plates H and H' are charged to equal and opposite potentials (usually 200 volts) as in Hankel's electroscope. The gold leaf is kept in the middle by means of the levelling-screws, and the sensitiveness (and stability) are easily altered by raising or lowering the leaf by means of the milled head M. The latter adjustment is the chief convenience of this electroscope. The sensitiveness of such an electroscope is a very indefinite thing; it depends upon the degree of instability of zero point and deflexion that one can permit, and this, in turn, depends on the greater or less protection of the case from rapid changes of temperature, currents of air, &c. This double electroscope appears to have some slight advantage over Wilson's form; when the two were mounted side by side under the same conditions the double electroscope had a sensitiveness about three times that of the tilted form, for equal stability. As used in the present experiments, the capacity of the leaf and its connexions was about 5 cm. and the sensitiveness was so adjusted as to give about 25 or 30 divisions on the scale in the

microscope for 0.1 volt. The key R, which was connected to a potentiometer arrangement, allowed the leaf to be insulated, grounded, or charged to any desired potential, and the volt-sensitiveness was taken immediately after each reading.

The case containing the aluminium foil electrode was exhausted, while the charcoal-bulb was heated, to a pressure of a few thousandths of a millimetre, and the bulb was cooled with liquid air. The bulb was between the case and the pump and thus formed a trap for the mercury vapour. Two litres of liquid air were used which lasted for about ten days. For that length of time the air-pressure could be kept continuously below .0001 mm. The pressure of the mercury vapour in the case must have been very small under these conditions. What vapour there was from the rubber stopcock grease used to cover the joint between the base-plate and cover must have been constantly distilling over from the case into the bulb; that its amount was small is shown by the fact that no visible traces of the grease could be seen in the charcoal-bulb after a week or more of this distillation, although in the same time drops of mercury of considerable size had distilled over from the pump.

When the  $\alpha$ -rays from the polonium were admitted into the case through the aluminium-covered holes in the top, both the insulated electrode and the case emitted electrons under their action. In order to separate the two effects it was necessary to charge the case; when it was charged positively, the electrons which were set free from the case were prevented from reaching the electrode, and the latter received a positive charge due to the loss of electrons from its two surfaces; when the case was charged negatively, the electrode received electrons from the case and emitted none itself. With +25 volts on the case the current of electrons from the aluminium foil was fully saturated, and it was not increased by the application of +200 volts. With +6 volts the lack of saturation was about 7 per cent. On the other hand, with a negative potential on the case it was distinctly more difficult to reach the saturation value; with -25 volts, the current was 20 per cent. less than with -200 volts. The probable cause for this difference will be discussed in the next paragraph.

When the case was charged negatively, the current was approximately twice as great as when the case was charged positively. Thus, apparently twice as many electrons were emitted by the case under the influence of the  $\alpha$ -rays as from the two sides of the aluminium-foil electrode through which

the rays passed. This difference persisted when the case itself was lined with aluminium foil, so it was not due to a specific difference between aluminium and brass. It is probable that the explanation of this difference as well as the difficulty in obtaining negative saturation mentioned in the last paragraph is to be found in the construction of the cover and the apertures through which the rays enter the exhausted chamber. Many of the rays, passing in a divergent pencil through the aluminium foil which covers the holes, strike the sides of the holes and do not reach the electrode. They thus liberate a number of electrons from the case and no corresponding ones from the electrode; and to draw all of these superfluous electrons from the small apertures in the top of the cover requires a considerably greater potential-difference than when they come from the electrode.

In order to find out whether the observed currents really had their source in the metals and were not due to residual gas or vapour, the foil was removed from the ring electrode. (The apertures in the top of the cover were so placed that the geometrical beam of rays fell entirely within the ring.) Under these conditions, the current with the case charged positively fell to 4 per cent. of its former value, while with a negative potential on the case the current was 90 per cent. of what it had been before. This slight falling off in the negative current was doubtless due to the fact that the ring electrode was less efficient in catching electrons from the case than when it was covered with foil. Of the small positive current, part at least was due to the rays which struck the brass rod which supported the ring (see fig. 1), so that we may be quite sure that the gas-effect contributes not more than 2 or 3 per cent. to the currents observed with this apparatus. The absence of positive particles justifies the further conclusion that the effect produced by the  $\alpha$ -rays on a metal consists in the direct expulsion of electrons, and not of neutral pairs which afterwards break up. As will be seen later, there is a very close relationship between this metal effect and the ordinary ionization of gases by  $\alpha$ -rays; and the result just given renders it at least unlikely that neutral pairs are emitted when gases are ionized by  $\alpha$ -rays as has been sometimes assumed in the case of other ionizing agents.

A further test of the relative importance of the metal and gas effects was made by measuring the current at different gas pressures up to 0.2 mm. The result may be expressed by the linear formula

$$i = A + Bp,$$



where  $i$  is the current,  $p$  the pressure, and A and B are constants. In the apparatus described,  $Bp$  was equal to A when  $p = \cdot 068$  mm., so that even with a pressure of several thousandths of a millimetre, the gas effect was small in comparison with the metal effect.

The above measurements (which were incidental and somewhat rough) permit an estimate of the number of electrons emitted when one  $\alpha$ -particle passes through the aluminium foil electrode. The  $\alpha$ -rays were at a point in their range corresponding to a distance in air from the polonium of 2.07 cm. At this point in the range Geiger's \* results show that an  $\alpha$ -particle produces about 4000 ions per mm. of its path in air at standard pressure. In the present case, the depth of the ionization-chamber was 40 mm.; most of the rays passed through somewhat obliquely and the average distance traversed was about 45 mm. At a pressure of  $\cdot 068$  mm. the ions per  $\alpha$ -particle would be

$$4000 \frac{45 \times \cdot 068}{760} = 16.$$

Half of these (the positives) reached the electrode and gave an effect equal to that of the electrons which left it. The number of electrons leaving both sides of the foil for each  $\alpha$ -particle passing through it is thus approximately eight †.

The foregoing preliminary experiments having shown that the effects observed in the electroscope were due to the emission of electrons from the surfaces of the metal, the speed of the  $\alpha$ -particles was varied by interposing sheets of aluminium foil between the polonium and the cover of the exhausted chamber. Foils of two different thicknesses were used; the thinner was  $0.64 \times 10^{-4}$  cm. in thickness and its approximate air-equivalent, according to Taylor's results, was 0.116 cm.; the other was  $3.2 \times 10^{-4}$  cm. thick and was equivalent to 0.58 cm. of air; it happened to be just five times as thick as the first foil.

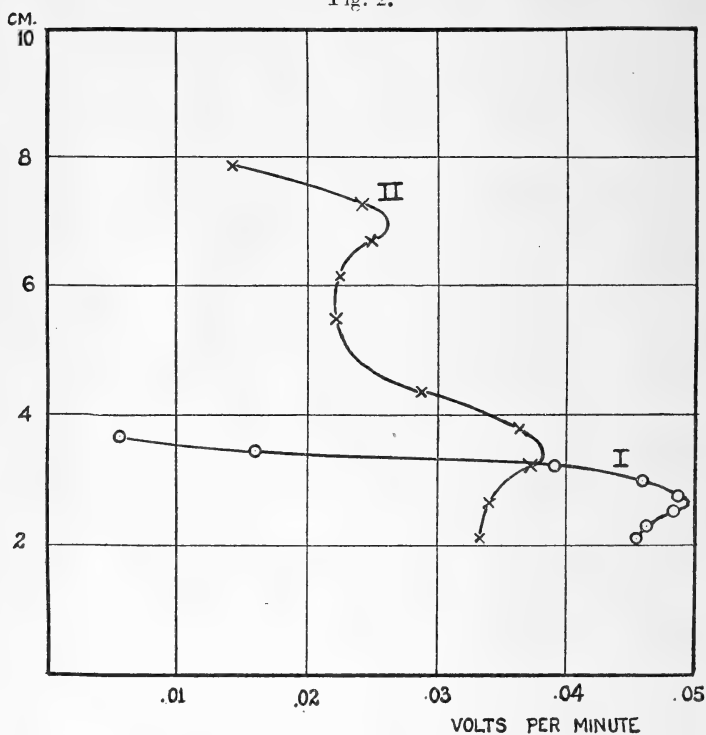
With the case charged to + 40 volts, the current of electrons from the electrode was measured as successive layers of foil were interposed. The current increased until five or six of the thin foils had been added, after which it

\* Proc. Roy. Soc. lxxxii. p. 486 (1909).

† Hauser, *Phys. Zeitsch.* xii. p. 466 (1911), whose paper appeared after the completion of these experiments, finds that about 20 electrons are emitted from one side (the emergence side) of an aluminium foil for each  $\alpha$ -particle.

rapidly decreased. Curve I. (fig. 2) shows the result of a series of such measurements made on Jan. 12, 1911. In the

Fig. 2.



Curve I. Polonium.

Curve II. Thorium Active Deposit.

figure, the currents in volts per minute are plotted as abscissæ, and the number of layers of foil as ordinates; in order to facilitate comparison with the ionization curve of polonium, however, the scale of ordinates indicates the air-equivalents of the foils. Each plotted point is the mean of from three to six separate observations, taken in various orders and with frequent returns to the measurement of the current with no foils, to check the constancy of the electro-scope readings. Several repetitions of these measurements gave entirely similar results.

Before entering the case the  $\alpha$ -rays passed through 0.6 cm. of air and through the thick aluminium foil which covered the holes in the top and whose air-equivalent was 1.47 cm., so that, with this apparatus, only the upper part of the

polonium curve can be obtained. To obtain  $\alpha$ -rays of greater range, I used the active deposit from the thorium emanation which emits  $\alpha$ -rays of two different speeds; the rays from thorium B have a range in air of 5.0 cm., and those from thorium C, of 8.6 cm. An additional advantage is the slow rate of decay of the thorium active deposit which falls to half value in 10.6 hours.

A small quantity ("activity of 2.4 mg.  $\text{RaBr}_2$ ") of Professor Hahn's mesothorium, obtained from Knöfler & Co. of Berlin, was available. This was placed in a small cylindrical cup of platinum with a hemispherical bottom, and was slightly moistened to increase its emanating power. The top of the cup was closed with a rather thick stopper of ebonite, in the centre of which was a hole through which passed a copper plug of the same dimensions as that on which the polonium had been deposited (4 mm. in diameter). The lower end of this plug was flush with the bottom of the ebonite stopper which was about halfway between the top and bottom of the cup. By this arrangement, when the cup was charged to +80 volts with respect to the copper plug, most of the lines of force which passed through the emanation fell upon the end of the plug and the greater part of the active deposit was collected there. After an exposure of 24 hours the accumulated deposit was sufficient to give very good readings in the apparatus described above, though somewhat less than had been obtained with the polonium. As there is an appreciable amount of radium with the mesothorium, it is necessary to wait about two or three hours before beginning measurements, in order to allow the radium active deposit to decay to a small value.

Series of observations were made in the same manner as with the polonium except that the thicker aluminium foil alone was used. On account of the decay of the active deposit it was necessary to complete a series within a reasonable number of hours, and it was desirable to repeat each measurement several times to guard against possible vagaries of the electroscope. Each reading was corrected in the usual manner for the decay of the active deposit. Curve II. (fig. 2) shows the result of the series of Mar. 9, 1911, which is typical of other similar series. The two "knees" are distinctly shown and their position is in excellent agreement with the ionization curve in air given by Hahn\*.

It appears from these experiments that (as was anticipated) the secondary  $\delta$ -radiation from the aluminium varies with

\* *Phys. Zeitsch.* vii. p. 415 (1906).

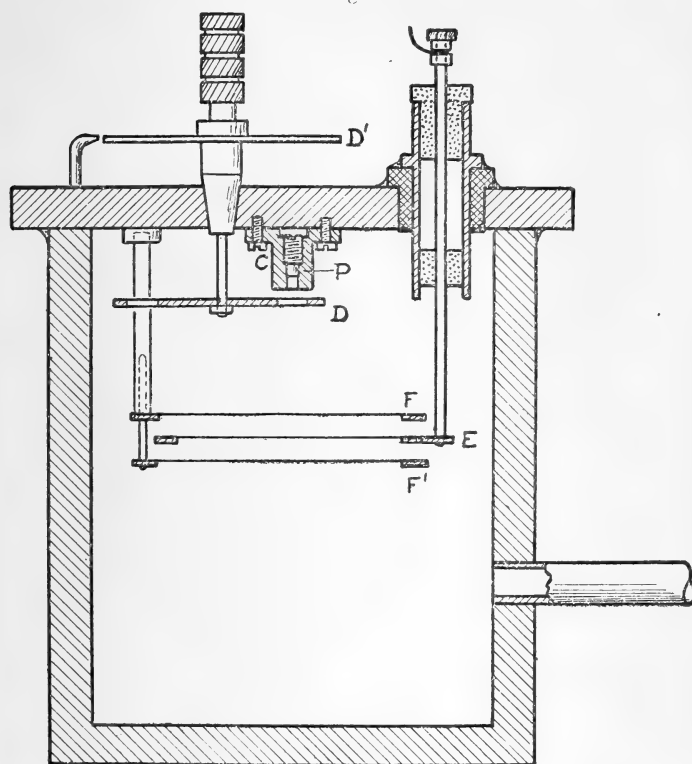
the speed of the  $\alpha$ -rays producing it in a manner entirely analogous to the variation in the gaseous ionization under like conditions. But the possibility of an error in this conclusion here suggests itself. When the  $\alpha$ -particle is not near the end of its range it passes through the thin aluminium electrode and the latter receives its positive charge solely on account of the electrons emitted by it. Near the end of the range, however, some of the  $\alpha$ -particles (those entering most obliquely) will stop in the foil, and it is possible that the observed increase in the positive charge acquired by the electrode is due to the positive charges on these  $\alpha$ -particles and not to any true increase in the  $\delta$ -radiation. It is easy to test this by charging the case negatively and measuring the negative charge received by the electrode from the electrons emitted by the case, for under these circumstances the stoppage of  $\alpha$ -particles by the electrode would decrease, instead of increasing, the effect. Unfortunately when this was tried a decisive result was not obtained. The current observed in the electroscope remained nearly constant while several foils were interposed and then fell off more gradually than with the positive charge on the case. As will be shown in the following pages, however, this was not due to the cause suggested above, but was in all probability the result of the construction of the chamber. As has been pointed out, many of the  $\alpha$ -rays must have struck the sides of the holes in the top at various angles up to grazing incidence. Thus the electrons emitted from the case were not all produced by particles moving with approximately the same speed, but by particles whose velocities varied considerably. Hence the effect was somewhat analogous to ionization curves obtained when the pencil of rays is not limited to a small angle by a "Bragg screen."

However, it was necessary to investigate the matter further. As a more intense source of radiation was desirable, Professor Boltwood was good enough to attempt the preparation of a much stronger deposit of polonium. By a special method he succeeded in depositing upon a 4 mm. plug as much polonium as would be in equilibrium with about 0.6 mg. of radium, and yet having so little foreign material with it that it appeared as a mere discoloration upon the copper. With this preparation, the difficulties of the experiment were greatly lessened; an electrometer could be used instead of the electroscope and much larger and steadier readings could be obtained.

In order to avoid the difficulties mentioned above, which prevented satisfactory readings when a negative potential

was put on the case, the experimental arrangements were altered.

Fig. 3.



CENTIMETERS  
0 1 2 3 4 5

The polonium-coated plug P (fig. 3) is placed within the evacuated chamber ; it is surrounded by a brass cylinder C, whose opening limits the cone of rays so that they fall within the ring E which supports the aluminium-leaf electrode. Two other rings F and F' above and below the electrode at a distance of 7 mm. are also covered with the aluminium leaf ; they are in metallic connexion with each other and with the case. The brass disk D is divided into six equal sectors ; one of these is left blank so that the rays may be stopped, while the five others have holes through them 1.3 cm. in diameter. These five holes are covered respectively with 2,

3, 4, 5, and 6 layers of the thicker aluminium foil whose air-equivalent is  $\cdot 58$  cm. The disk can be rotated about its axis which passes through the cover-plate with a cone bearing, made tight by rubber stopcock grease. A dial, D', enables one to set the disk so that the different layers of foil are interposed, or the rays stopped altogether by the blank sector. The electrode is insulated from the case by amber, guard-tube, and ebonite, and the joints made tight by sealing-wax; it was connected with a Dolezalek electrometer which, with 80 volts on the needle, had a sensitiveness of about 650 mm. divisions per volt. It was necessary to reduce somewhat the current-sensitiveness of the instrument; for this purpose a small mica condenser of about 150 cm. capacity was put in parallel with the electrometer.

With a positive potential on the case, the saturation current was reached with 40 volts; and when the brass sector was interposed in the path of the rays the current fell to a negligible value. On the other hand, it was impossible to approach saturation with a negative potential on the case, even at  $-320$  volts; the negative current when the rays were stopped by the disk was always large (20–40 per cent. of the total) and increased with the negative potential on the case. This part of the current was due to the electrons set free between the polonium and the disk; by subtracting this from the currents obtained with the foils interposed it was possible to eliminate this disturbing portion of the negative current. What was left consisted of the electrons from the two foils on the rings F, F', and from the surfaces of the disk-foils furthest from the polonium.

With this apparatus, practically identical results were obtained whether the case was charged positively or negatively; that is to say, whether the electrode emitted electrons or received those given off by the other aluminium foils. In the following table (p. 919), the results of various series of measurements are given. In order to facilitate comparison the currents are reduced to the same scale, that obtained with 2 foils (the smallest number used) being taken as 100 in each case.

These results leave no doubt, I think, that the increase in the secondary  $\delta$ -radiation is real, and is not due to the charge on the  $\alpha$ -particles themselves. The discrepancy between the positive and negative currents when six foils are interposed is easily explained. With a negative charge many of the electrons come from the foil on the disk D; with a positive charge they all come from the electrode E, and to reach this the  $\alpha$ -rays must penetrate the foil F (air-equivalent =  $0\cdot 116$  cm.). With 6 foils interposed we are in

TABLE I.

Date.	Volts on Case.	Number of Foils.				
		2.	3.	4.	5.	6.
May 23 .....	+160	100	107.2	118.5	107	39
„ .....	-160	100	104	118.2	107	54
May 27 .....	+ 80	100	104.5	116.2	106.8	38.7
„ .....	- 80	100	104.6	119	108.6	55.5
June 9 .....	+ 80	100	106	118	109	39.5
„ .....	- 80	100	104.5	119	110	51.8

the nearly horizontal “top” of the curve, and a small difference in the range makes a considerable difference in the effect\*.

In order to test the effect with another metal, three gold leaves were put upon the rings E, F, and F' instead of aluminium. These leaves were  $0.09 \times 10^{-4}$  cm. thick and had an air-equivalent of approximately 0.05 cm. (about half of that of the aluminium leaf). The emission from the gold

\* An effect probably due to this increased emission of electrons with diminishing speed of the  $\alpha$ -particles was observed by Aschkinass (*Ann. d. Phys.* xxvii. p. 377 (1908)). He was measuring the charge of the  $\alpha$ -particles after passing through various thicknesses of aluminium, and had a transverse magnetic field to curl up the  $\delta$ -rays. The  $\alpha$ -rays passed through an aluminium window into a separate chamber and fell upon a copper plate. Even without a magnetic field the plate acquired a positive charge; when a small thickness of aluminium was in the path of the rays, the magnetic field increased this positive charge, but only slightly (evidently the number of electrons emitted by the window and falling upon the plate was in excess of the number emitted by the plate itself but this excess was not enough to neutralize the charge carried by the  $\alpha$ -rays). When the  $\alpha$ -rays had to pass through a thicker layer of aluminium, the application of the magnetic field *diminished* the positive charge acquired by the plate (in this case, the electrons emitted by the plate appear to be in excess of those received from the window). The author draws the conclusion that “with diminishing speed of the primary  $\alpha$ -particles, it appears that the intensity of the secondary radiation increases, at first slowly, and finally considerably.” It does not appear that the conclusion is altogether justified by the experiment; the  $\delta$ -radiation from the window seems to have been left out of consideration; the most that can be concluded is that there is a differential effect as between copper and aluminium.

Another effect which is doubtless due to the same cause was observed by Duane (*C. R.* clxvi. p. 1088 (1908)). He found that the secondary radiation ceases a little less abruptly at the end of the range than the charge on the  $\alpha$ -particles. As he used an unlimited beam of rays, this result may well have been due to the increased emission of electrons near the end of the range.

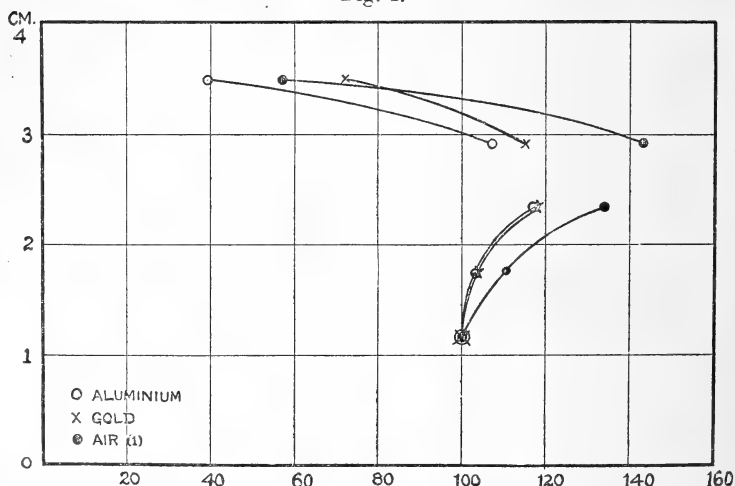
electrode was about 13 per cent. less than from the aluminium but the variation with the speed of the  $\alpha$ -rays was very nearly the same. In the following table are given the averages for all the experiments with both metals (with positive potential on the case); the currents with 2 foils are called 100 as before. Included in the table are two series of ionization measurements. These were made by removing the foil from the electrode E, admitting a small quantity of air (pressure  $\cdot 032$  mm.), and charging the case positively. The first of the two ionization measurements is with the aluminium leaf on F and F', the second with the gold leaf.

TABLE II.

No. of Foils.	2.	3.	4.	5.	6.
Al .....	100	105.2	117.6	107.3	39.1
Gold .....	100	105.6	118.2	115.6	72.2
Air (1) .....	100	110.5	134	143	57.3
Air (2) .....	100	110	130	143	96.5

As will be seen, the course of the series with the two metals is nearly identical; the differences in the last column are to be attributed to the greater stopping-power of the aluminium leaf; it appears also in the two ionization experiments with

Fig. 4.



the two metals on the ring F. Fig. 4 gives a graphical representation of these results; it is to be remembered,



however, that the ordinates of the different curves are not exactly adjusted to each other, on account of the differences just mentioned. It is indeed impossible to make satisfactory correction for these differences without knowing the relative values of the "incidence" and "emergence"  $\delta$ -radiation; for, between the generation of the two, the  $\alpha$ -rays pass through the leaf on the electrode, in the one case aluminium, in the other case gold. It is plain, however, that this correction (if it could be made) would bring closer together the two curves in their decreasing portions, while it would not much affect their increasing portions where they are already in close agreement.

The results of Taylor, mentioned at the beginning of this paper, would lead us to expect that the metal curves would lie to the left of the air-curve and have a less pronounced knee, as appears to be the case. But they give equal grounds for anticipating that the gold curve should be to the left of that obtained with aluminium, and this is not confirmed by the experiments. Quite apart from these somewhat hypothetical considerations it does not appear probable that two metals which differ so much in atomic weight and in other properties should give effects so nearly identical; the ionization curves in different gases are markedly different even when the gases differ much less from each other than gold and aluminium. The close similarity observed with the two metals gives rise to the suspicion that the electrons we have been measuring are emitted, not from the metals themselves, but perhaps from a layer of adsorbed gas which is the same in both cases. I have not yet had an opportunity to test this possibility, or to obtain the "ionization curves" of other metals, but I hope to do so shortly. The observation of Aschkinass (p. 919, footnote) seems to indicate that copper and aluminium would not give identical results.

### *Conclusions.*

1. The emission of electrons by aluminium and gold foils under the influence of  $\alpha$ -rays (secondary  $\delta$ -rays) varies with the speed of the  $\alpha$ -rays in a manner entirely analogous to the variation in the gaseous ionization produced by  $\alpha$ -rays. The emission at first increases and then rapidly decreases as the  $\alpha$ -rays near the end of their range, and the curves obtained show all the characteristics of the ionization curves in gases first obtained by Bragg.

2. The curves lie within (to the left of) the corresponding curves for gases and have a less conspicuous "knee." So

far they are in agreement with the known results on the retardation of  $\alpha$ -rays by metals, and with the hypothesis that the loss of energy by the  $\alpha$ -particles is due to an ionization of the metallic molecules. But the close similarity in the behaviour of gold and aluminium is not in accordance with this view.

3. In view of the dissimilarity in the ionization curves of different gases, the agreement in the curves obtained for aluminium and gold is unexpected, and leads to the suspicion that the observed effects may not be due to the metals themselves, but perhaps to a layer of adsorbed gas in both cases. A further investigation of this question will be undertaken shortly.

Sloane Laboratory,  
Yale University.  
August, 1911.

LXXXVIII. *On a Relation between the Atomic Volumes and the Spectra of Elements.* By R. ROSSI, M.Sc.\*

OF the recent theories explaining the possible origin of series of lines in spectra, the one which most seems to agree with experimental facts is due to Ritz †.

Ritz considers an electron vibrating in a magnetic field of strength  $H$ , the frequency of vibration being

$$\nu = \frac{e}{mc} H,$$

where  $\frac{e}{mc}$  is the ratio of the charge to the mass of the electron in electromagnetic units. The field  $H$  can be ascribed to elementary molecular magnets in a line, the electron being on their axis, at a distance  $r$  from the nearest pole. The field is then expressed by

$$H = \pm \mu \left( \frac{1}{r^2} - \frac{1}{(r+l)^2} \right),$$

$\pm \mu$  being the magnetic charge on each pole,  $l$  the length of the magnet, supposed to be made up by these elementary magnets. If  $l = ns$ , where  $n$  is an integer and  $s$  the length of an elementary magnet, and if we write  $r = as$  we get

\* Communicated by Prof. E. Rutherford, F.R.S.

† 'Magnetische Atomfelder und Serienspektren,' *Ann. der Physik*, xxv. p. 660 (1908).

$$\nu = \frac{e}{mc} \frac{\mu}{s^2} \left[ \frac{1}{a^2} - \frac{1}{(a+n)^2} \right], \quad n=1, 2, 3, \dots$$

an expression almost identical with

$$\nu = N_0 \left( \frac{1}{a} - \frac{1}{(b+n)^2} \right),$$

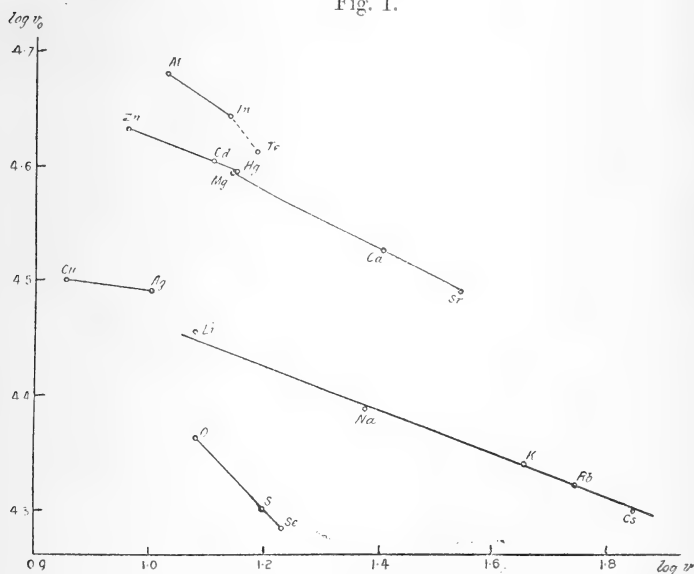
being Rydberg's formula to represent a series of lines in spectra;  $a$  and  $b$  are constant for each element,  $N_0$  is constant for all elements. Both formulæ approach a limit for  $n=\infty$ , and we should expect  $\frac{\mu}{s^2}$  equal for all elements.

The limit approached by Ritz's equation is

$$\nu_0 = \frac{e}{mc} \frac{\mu}{s^2} \frac{1}{a^2},$$

which is the root of the spectrum series.  $a$  is the ratio of the distance of the electron from the nearest magnetic pole to the length of one of these elementary magnets. We might expect this ratio, or consequently the root of the series  $\nu_0$ , to be some function of some atomic dimension. This seems to be the case, for if we plot on two orthogonal axes the logarithms of the roots of the series and of the

Fig. 1.



atomic volumes, the points representing elements of the same family lie very nearly in a straight line (fig. 1). In other

words, for every group of elements the root of the series can be expressed by

$$\nu_0 = Av^{-B},$$

$\nu$  being the atomic volume,  $A$  and  $B$  constants.

Thallium falls out of this rule altogether, and in the following calculations was neglected. Table I. gives the values of  $\frac{\log \nu_0 - \log A}{\log \nu}$  to show the deviations from the above law.

TABLE I.

Li ·166	Cu { Ag } ·049	Mg ·277	Al { In } ·220	Zn ·157	O ·516
Na ·179		Ca ·274		Cd ·156	S ·518
K ·176		Sr ·275	Tl ...	Hg ·157	Se ·517
Rb ·178					
Cs ·181					

$\nu_0$  is the mean of the roots of the two branch series, and was taken from Kayser's *Handbuch der Spectroscopie*; the atomic volumes were taken from Meyer's 'Theoretical Chemistry.' The deviations are rather large for Li and Na, but otherwise fall within the limits of the possible error made in the determination of the factors necessary for the calculation of the atomic volumes (atomic weight and specific gravity).

The following (Table II.) are the values of the constants  $A$  and  $B$  for the different families of elements.

TABLE II.

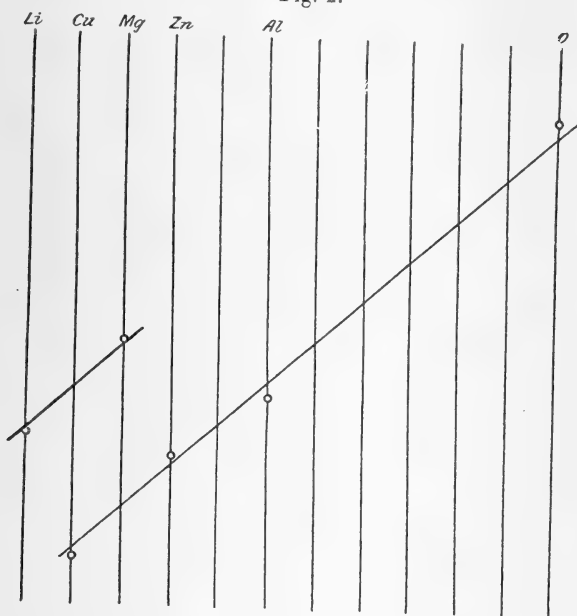
	Li, Na, K, Rb, Cs.	Cu, Ag.	Mg, Ca, Sr.	Zn, Cd, Hg.	Al, In.	O, S, Se.
A ...	43150	34910	82600	60310	81100	83560
B ...	·177	·049	·275	·157	·220	·517

For the trunk series of the alkali metals, the deviations from the above law are even larger than for the branch series, and it is therefore doubtful whether such relation should hold for the trunk series also. It may, however, be remembered that, through the Rydberg-Schuster law, the common root  $\nu_0$  of the two branch series which we have so far been considering also represents the range of frequencies of the

trunk series, so that the latter also is indirectly connected in some way with the above atomic volumes' law.

It was next tried to find a law connecting the two constants A and B. The larger A, the larger is B, but they cannot be connected by any simple mathematical relation. B seems to be increasing by a definite amount as we pass from group to group. For if we draw some parallel equidistant lines representing the different families of elements (corresponding to the vertical columns of Mendeléeff's tables) and plot on these the values of B, we find that the points thus obtained lie near two parallel lines (fig. 2).

Fig. 2.



In conclusion, the constant  $a$  of Ritz's formula can be expressed as a function of the atomic volume, so that whether these fields of magnetic force are due to elementary magnets, or as imagined by Ritz to solids of revolution charged with electricity at their surface and in rapid rotation round their axis, there seems to be a connexion between their dimensions or configurations and the volume of the atom containing them.

Manchester University,  
October 1911.

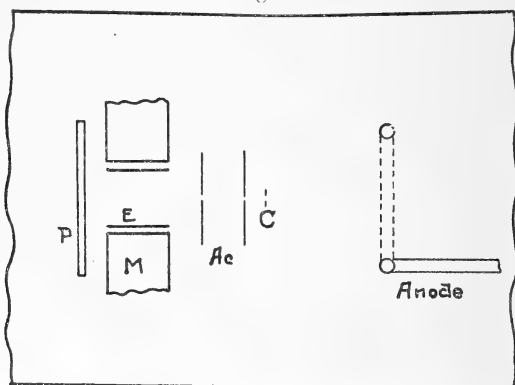
LXXXIX. *Rays of Positive Electricity from the Wehnelt Cathode. A Preliminary Note. By CHAS. T. KNIPP, Ph.D., Assistant Professor of Physics in the University of Illinois, U.S.A.\**

[Plate XVII.]

THE object of this note is to describe briefly the work that has been in progress at the Cavendish Laboratory during the past year, on the measurement of the properties of the Canalstrahlen when a Wehnelt or hot lime cathode is employed. In 1904 Professor Wehnelt † observed these rays experimentally. Up to that time he was not able to get a sufficiently clear outline on the screen to enable him to make measurements.

The success attending the measurement of the rays ‡ of positive electricity, in the case of an ordinary perforated cathode, by putting the photographic plate inside the discharge tube suggested that the same method might be employed to advantage in measuring the properties of the slower moving carriers that are produced by the hot lime cathode. Earlier in the year numerous attempts were made to get photographic records in this way but without success. The inference was that if carriers are present they do not possess energy enough to affect the photographic plate. To overcome this difficulty I next arranged to increase their velocity by means of an accelerating condenser.

Fig. 1.



The general arrangement of the apparatus is sketched diagrammatically in fig. 1. It consists, briefly, of a hot

\* Communicated by Sir J. J. Thomson, F.R.S.

† A. Wehnelt, *Ann. d. Phys.* vol. xiv. p. 464.

‡ J. J. Thomson, *Phil. Mag.* vol. xviii. Dec. 1909; vol. xx, Oct. 1910; vol. xxi. Feb. 1911.

line cathode C, back of which is placed the accelerating condenser Ac. In line with these are placed the nearly coterminous magnetic and electrostatic fields. Beyond, and fairly close, is the photographic plate P. The diameter of the containing cylinder is about 9 cm. With this arrangement I got the first definite evidence of the positive carriers on June 1st of the present year, and photographs that admitted of exact measurement followed a few days later. It was soon observed that with high accelerating fields sharp photographs resulted only when the plate P is but a few cms. from the emerging beam. At 3 cm. the photographs are blurred and indistinct. To date, 26 photographic plates have been exposed under varying conditions of discharge, magnetic and electric fields, accelerating field, and distance of plate from the emerging beam. On many of the plates more than one exposure was made. Of the above number I have only 7 plates on which the lines are clearly enough cut to measure accurately.

The vacua employed were the highest that could be obtained by the aid of liquid air and charcoal. For these vacua, in the apparatus as I have it constructed, 15 to 18 hundred volts are required to start the discharge even though the platinum cathode be initially at a cherry-red heat. However, when once started, the terminal potential difference often dropped to one-quarter of the above value. Slight fluctuations in the heating current produced correspondingly large fluctuations in the discharge. This is due to the lime cathode evolving gas very freely when heated. In my apparatus the evolution of gas at white heat was much more rapid than the two charcoal bulbs in liquid air could absorb, in fact at times the charcoal seemed to refuse to absorb it at all.

The magnetic field was measured by means of a Grassot flux-meter and a triangular coil. The equation \* that applies is

$$I = \frac{nd}{l} \int_0^l (l-x) H dx,$$

where I is the magnetic induction through the coil as measured by the flux-meter.

For the electrostatic field I at first made use of the well-known equation †

$$x = \frac{e}{mv^2} X l \left( \frac{l}{2} + d \right) . . . . . (1$$

\* J. J. Thomson, *Phil. Mag.* Dec. 1909.

† J. J. Thomson, 'Conduction of Electricity through Gases,' 2nd ed. p. 121 (1906).

A much more accurate one would be given by the application of the Schwarzian transformation\* ; however, the necessarily large distance apart of the plates forming the boundaries of the electrostatic field makes the application of this transformation difficult if not quite impossible.

From the theory of the action of magnetic and electric fields on electrified carriers in motion we have the equations

$$v = \frac{y}{x} X \frac{K_1}{B} = \frac{y}{x} \frac{A}{B} = \frac{y}{x} C_1,$$

$$\frac{e}{m} = \frac{y^2}{x} \frac{A}{B} = \frac{y^2}{x} C_2,$$

where A and B are constants depending upon the electric and magnetic fields and the geometrical data of the discharge-tube. The constant A may be written as the product of two constants thus

$$A = XK_1,$$

where X is the potential difference divided by the distance between the plates, and  $K_1$  is a constant depending solely upon the geometrical data of the discharge-tube. For the reason stated above the value of  $K_1$  for my apparatus as given by equation (1) is in question. I determined it experimentally by passing a beam of cathode rays through the system and measured the electrostatic displacement on the photographic plate, and also the minimum spark potential required to produce this displacement. These together with

$$\frac{e}{m} = 1.7 \times 10^7$$

for cathode rays gave the value

$$K_1 \text{ (corrected)} = 1.87,$$

against

$$K_1 \text{ (uncorrected)} = 1.8.$$

The corrected value of  $K_1$  was used in the calculation of the data that follow.

All the photographs show two and on several plates three and four lines. These vary greatly in sharpness and intensity from plate to plate. Two types of curves were obtained. First those that are straight lines passing out from the origin, and second parabolas having their heads in the same vertical line.

Curves of the first type are the most likely to occur

\* J. J. Thomson, *Phil. Mag.* vol. xx, Oct. 1910.



especially if low potential differences are used in accelerating the carriers. The data relative to the two most prominent lines on plate 18 are as follows :—

$y_b$ .	$y_a$ .	$x$ .	Square of ratio.	$\frac{y_b}{x}$ .	$\frac{y_a}{x}$ .	$\frac{y_b^2}{x}$ .	$\frac{y_a^2}{x}$ .	$v_b \times 10^7$ .	$v_a \times 10^7$ .	$\left(\frac{e}{m}\right)_b \times 10^4$ .	$\left(\frac{e}{m}\right)_a \times 10^4$ .
6.05	4.00	2.56	2.28	2.65	1.56	14.7	6.2	3.96	2.62	.86	.38
4.80	3.15	2.01	2.31	2.38	1.56	11.4	4.4	4.0	2.62	.63	.30
3.63	2.41	1.55	2.34	2.36	1.55	8.7	3.7	3.9	2.6	.32	.23
2.61	1.71	.98	2.34	2.66	1.74	6.9	2.9	4.4	2.9	.42	.18

In this photograph the accelerating and electric fields were 1158 and 153 volts respectively. The following data taken from plate 26 represent a set of curves that approach the second type. The corresponding accelerating and electric fields were 1548 and 171 volts.

$y_b$ .	$y_a$ .	$x$ .	Square of ratio.	$\frac{y_b}{x}$ .	$\frac{y_a}{x}$ .	$\frac{y_b^2}{x}$ .	$\frac{y_a^2}{x}$ .	$v_b \times 10^7$ .	$v_a \times 10^7$ .	$\left(\frac{e}{m}\right)_b \times 10^4$ .	$\left(\frac{e}{m}\right)_a \times 10^4$ .
.....	4.97	2.65	.....	.....	1.87	.....	9.32	.....	3.0	.....	.51
.....	4.49	2.20	.....	.....	2.0	.....	9.16	.....	3.3	.....	.50
5.52	3.89	1.74	2.01	3.17	2.24	17.5	8.79	5.1	3.6	.96	.48
4.80	3.48	1.40	1.90	3.4	2.5	16.3	8.65	5.6	4.0	.91	.47

From an inspection of the table for plate 18 we see that the velocity of the carriers remains constant as  $x$  and  $\frac{e}{m}$  increase; however, in plate 26 the velocity falls off as  $x$  increases while  $\frac{e}{m}$  remains (nearly) constant. To get curves of type 2 it is necessary to use a stronger accelerating field. The stronger this field the nearer the heads of the parabolas are pushed towards the origin. At this writing I have not been able to use fields above 1548 volts because of fogging due to internal sparking.

Plates 18, 20, 24 A, and 26 A are typical photographs, and are enlarged and reproduced in figs. 2, 3, 4, and 5 (Pl. XVII.).

For plate 20 (fig. 3) we have

	P.D. between plates...	= 156 volts,
	Ac-field.....	= 1093 „
Hence,	C <sub>1</sub> .....	= 1.52 „
	C <sub>2</sub> .....	= .5 „

The data for this plate corresponding to an electrostatic deflexion  $x = 4.5$  mm. are given in the following table :—

$v$ from curve $\times 10^7$ .	$v$ calc. $\times 10^7$ .	$\frac{e}{m} \times 10^4$ .	Elect. atomic weight.	Element.
3.12	4.55	.95	1.05	H+
2.15	3.10	.45	2.2	H <sub>2</sub> +
1.30	1.9	.166	6.0	C++
.77	1.1	.057	17.5	O+

In the above it should be remarked that there was some uncertainty in setting the measuring instrument on  $x$ . This set of curves belongs to type 1. The heads of the parabolas are shown but feebly in the photograph and not at all in the reproduction. It is interesting to note that the velocities given in the second column, calculated by means of the energy equation

$$1/2 mv^2 = eV,$$

are in each case greater (by about 40 per cent. for this plate) than the corresponding values given by measurements made on the curves. This is as it should be, for we expect the carriers to be slowed down considerably by impact with the molecules of the remaining gas in the tube. The fourth column contains the electric atomic weights\*. They show that the curves are most likely due to the hydrogen atom, the hydrogen molecule, the atom of carbon with two charges, and the atom of oxygen with one charge.

The results calculated from the measurements made on

\* J. J. Thomson, *Phil. Mag.* vol. xxi. p. 234, Feb. 1911.

photographic plate 26, the last plate exposed, are as follows :—

x in mm.	Curve.	Exposure a.				Exposure b.			
		v from curve $\times 10^7$ .	v calc. $\times 10^7$ .	$\frac{e}{m} \times 10^4$ .	Elec. atomic weight.	v from curve $\times 10^7$ .	v calc. $\times 10^7$ .	$\frac{e}{m} \times 10^4$ .	Elec. atomic weight.
1.40	b	5.6	5.3	.91	1.1	5.6	5.4	.94	1.06
	a	4.0	3.8	.47	2.1	4.0	3.8	.476	2.1
	a <sub>1</sub>	2.2	2.1	.14	7.1	2.43	2.3	.17	*5.88
	a <sub>2</sub>	1.8	1.2	.097	10.1				
1.74	b	5.1	5.4	.96	1.04				
	a	3.6	3.8	.48	2.08	3.89	4.1	.55	1.81
	a <sub>1</sub>	2.1	2.3	.17	*5.88	2.2	2.3	1.83	*5.4
	a <sub>2</sub>	.84	1.6	.025	40.0				
2.2	b								
	a	3.3	3.9	.50	2.0	3.2	3.8	.48	2.06
	a <sub>1</sub>	1.9	2.2	.16	7.2	1.9	2.3	.18	*5.5
	a <sub>2</sub>	1.0	1.2	.046	21.7	.95	1.0	.043	23.2
2.65	b								
	a	3.0	3.9	.51	1.96	3.1	4.1	.55	1.81
	a <sub>1</sub>	1.8	2.3	.18	5.5	1.8	2.3	.18	5.5
	a <sub>2</sub>	.89	1.1	.043	23.2	1.1	1.35	.059	17.0

Two successful exposures of 45 minutes each were made on this plate. I calculated the values of  $v$  and  $\frac{e}{m}$  for four distances taken at random from the  $y$ -axis. The curve  $a_1$  shows double at the distance  $x=1.74$  mm. in exposure  $a$ , and distinctly double, except at the extreme end, in exposure  $b$ . Note the calculated velocities given in the second column. Near the  $y$ -axis these values are less than the velocities calculated from the curve. This indicates that the curves are not parabolas as you approach the origin but degrade into straight lines. The data for both exposures show this.

Lastly I have collected in one table the electric atomic weights calculated from the curves on the seven photographic plates. Plates 21, 23, 24, and 26 have two exposures each. The values calculated for a given curve are placed in the same column even though they were in several instances smaller or larger than the average for that column. In plate 26 the values marked with an asterisk indicate single settings on a double curve. If a redistribution of the values in this table were made several would fall in adjacent

columns. Thus the value 6.58 should go to the adjacent column or even to the second adjacent one. Similarly the value 7.7 should be moved over two columns, and farther down 7.1 and 7.2 to the adjacent column. Again the value 17 at the bottom of the table might well represent oxygen and be moved one column back. The distributed places in the table are indicated by a †.

Plate.	x in mm.	ELECTRIC ATOMIC WEIGHT.									
17	2.65		2.3	6.58	†	†(?)					
"	3.84		1.66	4.54							
"	4.90		1.78	3.7							
18	3.38	1.05	3.2	...	...	...	...	12			
20	4.5	1.05	2.2	...	6	...	...	...	17		
21a	2.35	.97	2.27								
"	2.55	1.07	2.8								
"	2.57	1.03	2.1								
21b	2.35	.93	...								
23	1.84	...	2.1	4.7							
"	2.54	...	1.96	3.46	...	...	...	...	...	22.7	
"	3.34	...	2.17	3.46							
24a	1.48	...	2.2	...	7.7	...	†				
"	2.2	...	1.8	...	5.2						
"	2.86	...	1.6	4.7							
"	3.86	...	1.63	4.7							
24b	2.2	...	...	...	5.0						
26a	1.4	1.10	2.1	...	7.1	†					
"	1.74	1.04	2.08	...	*5.88		...	...	...	...	40
"	2.2	...	2.0	...	7.2	†	...	...	...	21.7	
"	2.65	...	1.96	...	5.5	...	...	...	...	23.2	
26b	1.4	1.06	2.1	...	*5.88						
"	1.74	...	1.81	...	*5.4						
"	2.2	...	2.06	...	*5.5	...	...	...	...	23	
"	2.65	...	1.81	...	5.5	...	...	...	†	17	
		H+	(H <sub>2</sub> )+	(?)	C++	N++	O++	C+	O+	(?)	(CO <sub>2</sub> )+
		1	2	(?)	6	7	8	12	16	(?)	44

Thus the photographs taken collectively show the two hydrogen lines, a line of atomic weight 4, the carbon atom with two charges, the carbon atom with one charge, the oxygen atom with one charge, another line that was visible on three different plates of atomic weight 22, and a final line corresponding to CO<sub>2</sub> with one charge.

#### *Summary.*

The present investigation may be summarized as follows:—

1. The velocity of the carriers of positive electricity in the case of the hot line cathode is not great enough to affect a photographic plate upon which they may strike.

2. These slow moving particles can be accelerated at will, the minimum potential difference required to give them a sufficient velocity to affect the plate being about 500 volts per centimetre.

3. There is secondary radiation present as well as primary—both straight lines and their continuations as parabolas are shown on a few of the photographs.

4. The value of  $e/m$  is the same for the various carriers as that found by Sir J. J. Thomson in the case of the positive rays formed by the ordinary perforated cathode with high potential discharge.

5. The greater the acceleration the more clearly cut and well defined are the photographs, also the nearer the parabolas extend to the origin.

6. This investigation does not show a negative counterpart to any of the curves.

7. The work thus far has been with residual air only.

In conclusion I wish to express my appreciation to Professor Sir J. J. Thomson for the problem and the main line of attack, also for the facilities of the Cavendish Laboratory that he so kindly placed at my disposal.

August 17, 1911.

*XC. On the Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions. By S. A. SHORTER, B.Sc., Assistant Lecturer in Physics in the University of Leeds.—Part I. The General Theory of Chemical Potential in a Binary System. Osmotic Pressure and Vapour-Pressure of Solutions\*.*

GIBBS'S Theory of Chemical Potential † is a very powerful instrument for the solution of many thermodynamical problems. This instrument, however, seems never to have been applied to the solution of many important problems in the Theory of Solutions. Thus many attempts have been made to deduce an expression connecting the osmotic pressure and vapour-pressure of a concentrated solution. Nearly all the expressions which have been deduced are approximate; one well-known expression is quite wrong. In only one case ‡ has an exact expression been deduced connecting the osmotic pressure and vapour-pressure of a

\* Communicated by the Author.

† "On the Equilibrium of Heterogeneous Substances," Collected Works, vol. i. p. 55.

‡ Porter, Roy. Soc. Proc. A. vol. lxxix. p. 519 (1907).

*Phil. Mag. S. 6. Vol. 22. No. 132. Dec. 1911.* 3 Q

solution of a single involatile solute. By means of the Theory of Chemical Potential an expression of a very general nature connecting the vapour-pressures of two solutions and the pressures under which they co-exist in osmotic equilibrium, can be deduced with extreme ease, not only in the special case of one involatile solute, but in the general case of any number of involatile solutes. Other problems, such as the conditions of co-existence of a liquid and vapour under different pressures (the effect of pressure on the vapour-pressure), the effect of gravity on a solution, &c., may also be solved in a simple manner by this method. The author proposes to treat these questions in a later communication.

*Summary of Notation.*

The following are the chief symbols used in this paper :—

$M_0$  the mass of the solvent  $S_0$  ;

$M_1$  the mass of the solute  $S_1$  ;

$S = \frac{M_1}{M_0}$  the concentration of the solution ;

$W$  the volume of the solution ;

$\Pi_0$  the vapour-pressure of the pure solvent ;

$\Pi$  the vapour-pressure of the solution ;

$v(s, p, \theta)$  the specific volume of a solution of concentration  $s$  at a temperature  $\theta$  and under a pressure  $p$  ;

$v(0, p, \theta)$  the specific volume of the pure solvent ;

$f_0(s, p, \theta)$  the chemical potential of the solvent in a solution of concentration  $s$  at a temperature  $\theta$  and under a pressure  $p$  ;

$f_1(s, p, \theta)$  the chemical potential of the solute in the solution ;

$f_0(0, p, \theta)$  the chemical potential of the solvent in the pure liquid state ;

$P_0(s, p, \theta) \equiv \frac{\partial}{\partial p} f_0(s, p, \theta) ;$

$F_0(p, \theta)$  the chemical potential of the solvent in the pure vapour state ;

$V(p, \theta)$  the specific volume of the solvent vapour ;

$\Omega(s, p, \theta)$  the osmotic pressure of a solution of concentration  $s$  at a temperature  $\theta$ , when the pressure on the pure solvent is  $p$ .

The symbols  $v, f_0, P_0$ , &c., will sometimes be used alone when there is no doubt as to the particular values of the variables involved.

*The Theory of Chemical Potential in a Binary System.*

Before considering the applications of the Theory of Chemical Potential, we will give a brief account of Duhem's \* development of the theory in a binary system.

If the external generalized forces acting on a system are constant, the condition for equilibrium may be expressed in the following manner :—

Let  $U$  denote the internal energy of the system,  $\theta$  the absolute temperature,  $\phi$  the entropy, and  $\psi$  the potential of the external generalized forces (*i. e.* the sum of the products of the forces and the corresponding generalized coordinates), and let

$$\Phi = U - \theta\phi - \psi.$$

The necessary and sufficient condition for equilibrium is that in any virtual isothermal modification of the system

$$\delta\Phi \geq 0.$$

The function  $\Phi$  is called by Duhem the Total Thermodynamical Potential of the system.

Consider a homogeneous system containing two components,  $S_0$ , which will be called the solvent, and  $S_1$ , which will be called the solute. Let the masses of these components be  $M_0$  and  $M_1$  respectively. Let the volume of the system be  $W$ , and suppose it to be subjected to a uniform pressure  $p$ . Then we have

$$\Phi = U - \theta\phi + pW.$$

If we consider  $\Phi$  as a function of  $M_0$ ,  $M_1$ ,  $p$ ,  $\theta$  it will be homogeneous of the first degree in  $M_0$  and  $M_1$ , and can therefore be written in the form

$$\frac{\partial\Phi}{\partial M_0} M_0 + \frac{\partial\Phi}{\partial M_1} M_1.$$

Now  $\frac{\partial\Phi}{\partial M_0}$  and  $\frac{\partial\Phi}{\partial M_1}$  will be homogeneous functions of  $M_0$  and  $M_1$  of zero degree, and can therefore be written in the forms  $f_0(s, p, \theta)$  and  $f_1(s, p, \theta)$  respectively, where  $s = \frac{M_1}{M_0}$ . Since evidently

$$\frac{\partial}{\partial M_1} \frac{\partial\Phi}{\partial M_0} = \frac{\partial}{\partial M_0} \frac{\partial\Phi}{\partial M_1},$$

it can easily be proved that

$$\frac{\partial f_0}{\partial s} = -s \frac{\partial f_1}{\partial s}.$$

\* *La Mécanique Chimique*, vol. iii. pp. 1-10.

Consider two homogeneous systems at the same temperature and under the same pressure, the first containing masses  $M_0$  and  $M_1 + \delta M_1$  respectively of the components  $S_0$  and  $S_1$ , and the second masses  $M_0$  and  $M_1 - \delta M_1$ . If these two systems are put into communication we shall have finally a homogeneous system containing masses  $2M_0$  and  $2M_1$  of the components. This irreversible process of uniform mixing must result in a diminution of the total thermodynamical potential, so that we must have

$$\Phi(2M_0, 2M_1, p, \theta) < \Phi(M_0, M_1 + \delta M_1, p, \theta) + \Phi(M_0, M_1 - \delta M_1, p, \theta).$$

From this we may readily prove the inequalities

$$\frac{\partial}{\partial s} f_1(s, p, \theta) > 0,$$

$$\frac{\partial}{\partial s} f_0(s, p, \theta) < 0.$$

If  $v(s, p, \theta)$  denotes the specific volume of the solution we have

$$\frac{\partial \Phi}{\partial p} = (M_0 + M_1)v(s, p, \theta).$$

By differentiating this equation with respect to  $M_0$  and introducing the variable  $s$ , we obtain the equation

$$\frac{\partial}{\partial p} f_0(s, p, \theta) = v(s, p, \theta) - s(1+s) \frac{\partial}{\partial s} v(s, p, \theta).$$

The value of  $\frac{\partial f_1}{\partial p}$  may be obtained in a similar manner.

The functions  $f_0(s, p, \theta)$  and  $f_1(s, p, \theta)$  are called the chemical potentials of the components of the system. The importance of the chemical potential lies in the fact that if a system consists of two or more homogeneous parts in equilibrium, the chemical potential of any component must be the same in all parts of the system, so long as the motion of a quantity of that component from one part to the other is a possible virtual modification of the system. This follows from the general condition of equilibrium.

*The Effect of a Finite Change of Pressure on the Chemical Potential of the Solvent in the Solution.*

In the previous section we have shown that the value of  $\frac{\partial}{\partial p} f_0(s, p, \theta)$  can be calculated from simple experimental data.



As this quantity plays a very important part in the subsequent theory, it will be denoted by the special symbol  $P_0(s, p, \theta)$ . If the volume  $W$  of the solution is regarded as a function of  $M_0$ ,  $M_1$ ,  $p$ , and  $\theta$ , it can be shown that

$$\frac{\partial W}{\partial M_0} = P_0(s, p, \theta).$$

This quantity is evidently positive and of the same order of magnitude as the specific volume of the pure solvent. In cases where the change of volume on solution is small the two quantities are approximately equal.

In the case of a liquid mixture, the changes of pressure involved in the phenomena under consideration cause only a very small change in the density, so that we have approximately

$$f_0(s, p_2, \theta) - f_0(s, p_1, \theta) = (p_2 - p_1)P_0(s, p_1, \theta).$$

If we write

$$P_0(s, p_1 \rightarrow p_2, \theta) = \frac{1}{p_2 - p_1} \int_{p_1}^{p_2} P_0(s, x, \theta) dx,$$

we have the exact equation

$$f_0(s, p_2, \theta) - f_0(s, p_1, \theta) = (p_2 - p_1)P_0(s, p_1 \rightarrow p_2, \theta) \quad (1)$$

The quantity  $P_0(s, p_1 \rightarrow p_2, \theta)$  may be called the mean value of  $P_0$  between the pressures  $p_1$  and  $p_2$ .

An expression for this mean value may be obtained if we assume that

$$v(s, p, \theta) = v(s, \varpi, \theta) \{1 - \beta(p - \varpi)\}$$

where  $\beta$  is the compressibility of the solution and  $\varpi$  any convenient pressure, which in this case we will assume to be atmospheric pressure, since the density measurements necessary for the calculation of  $P_0$  will have been made under atmospheric pressure.

Assuming that  $\frac{\partial P_0}{\partial p}$  is independent of the pressure it can readily be shown that

$$P_0(s, p_1 \rightarrow p_2, \theta) = P_0(s, \varpi, \theta) \left\{ 1 - \lambda \left( \frac{p_1 + p_2}{2} - \varpi \right) \right\} \quad (2)$$

where

$$\lambda = \beta - s(1 + s) \frac{v(s, \varpi, \theta)}{P_0(s, \varpi, \theta)} \frac{\partial \beta}{\partial s}.$$

In the special case where  $s=0$  the function  $P_0$  becomes equal to the specific volume of the pure solvent, and if we adopt a similar notation for the mean value of this latter quantity we have

$$v(0, p_1 \rightarrow p_2, \theta) = v(0, \varpi, \theta) \left\{ 1 - \beta_0 \left( \frac{p_1 + p_2}{2} - \varpi \right) \right\} \quad (3)$$

where  $\beta_0$  is the compressibility of the pure solvent.

### *The Thermodynamical Theory of Osmotic Pressure.*

Consider the pure solvent at a pressure  $p_0$  in equilibrium with the solution at a pressure  $p$ , the two being separated by a membrane permeable to the solvent only. The chemical potential of the solvent must have the same value in the solution as it has in the pure liquid state. Hence we have

$$f_0(0, p_0, \theta) = f_0(s, p, \theta).$$

Since the chemical potential of the solvent decreases with increase of concentration, and increases with increase of pressure,  $p$  must be greater than  $p_0$ . The difference  $p - p_0$  is determined as a function of  $s, p_0$ , and  $\theta$  by the above equation. We will denote this difference by  $\Omega(s, p_0, \theta)$ , or by  $\Omega$  simply, when it is not necessary to specify the particular values of the variables. The above equation may be written in the form

$$f_0(0, p_0, \theta) = f_0(s, p_0 + \Omega, \theta) \quad (4)$$

The quantity  $\Omega(s, p_0, \theta)$  is usually called the osmotic pressure of the solution. This term is rather misleading, since given values of the temperature and concentration do not fix the value of  $\Omega$ . It is necessary to specify in addition the pure solvent pressure. The value of  $\frac{\partial}{\partial p_0} \Omega(s, p_0, \theta)$  is easily calculated. If an increase  $\delta p_0$  in the pure solvent pressure causes an increase  $\delta \Omega$  in the osmotic pressure, we have

$$f_0(0, p_0 + \delta p_0, \theta) = f_0(s, p_0 + \delta p_0 + \Omega + \delta \Omega, \theta).$$

Hence we have

$$\frac{\partial}{\partial p_0} \Omega(s, p_0, \theta) = \frac{v(0, p_0, \theta)}{P_0(s, p_0, \theta)} - 1.$$

The theory of chemical potential shows clearly that osmotic pressure cannot be regarded as a specific property of the solution. The osmotic pressure is simply the increase of pressure necessary to counteract the lowering effect of the addition of the solute on the chemical potential of the solvent.

The relation between this lowering effect and the compensating pressure increase is shown by the following equation, which may be derived from equation (4) by means of equation (1),

$$f_0(0, p_0, \theta) - f_0(s, p_0, \theta) = \Omega(s, p_0, \theta) P_0(s, p_0 \rightarrow p_0 + \Omega, \theta). \quad (5)$$

*The Thermodynamical Theory of Vapour-Pressure.*

If the pure liquid solvent and its vapour are in equilibrium, the surface of separation being plane, the pressure of the system is determined as a function of the temperature by the equation

$$f_0(0, \Pi_0, \theta) = F_0(\Pi_0, \theta) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $F_0(\Pi_0, \theta)$  is the chemical potential of the solvent vapour at a pressure  $\Pi_0$  and temperature  $\theta$ .

If the solution and the solvent vapour are similarly in equilibrium, the pressure is determined as a function of the temperature and concentration by the equation

$$f_0(s, \Pi, \theta) = F_0(\Pi, \theta). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If  $V(x, \theta)$  denotes the specific volume of the solvent vapour at a pressure  $x$  and temperature  $\theta$ , we have

$$\frac{\partial}{\partial x} F_0(x, \theta) = V(x, \theta).$$

Hence we have, from equations (6) and (7),

$$f_0(0, \Pi_0, \theta) - f_0(s, \Pi_0, \theta) = \int_{\Pi}^{\Pi_0} V(x, \theta) dx - (\Pi_0 - \Pi) P_0(s, \Pi \rightarrow \Pi_0, \theta). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Since  $V(x, \theta)$  is always greater than  $P_0(s, x, \theta)$ ,  $\Pi_0 - \Pi$  is always positive, *i. e.* the effect of the addition of the solute is to lower the vapour-pressure.

The lowering of the vapour-pressure and the osmotic pressure are both closely related to the lowering of the chemical potential of the solvent. A relation between the two will be deduced in the next section.

*The Relation between the Conditions of Osmotic Equilibrium and Vapour-Pressure.*

If we suppose that in the case of osmotic equilibrium between the solution and the pure solvent the latter is under

a pressure equal to its own vapour-pressure, equation (5) gives the value of  $f_0(0, \Pi_0, \theta) - f_0(s, \Pi_0, \theta)$  in terms of the osmotic pressure. If we equate this to the value given in equation (8) we immediately obtain a relation between this special osmotic pressure and the vapour-pressure. A much more general equation can, however, be deduced without difficulty. Suppose that we have a solution of concentration  $s$  under a pressure  $p$  in osmotic equilibrium with a solution of concentration  $s'$  under a pressure  $p'$ . Let  $\Pi$  and  $\Pi'$  be the respective vapour-pressures of the two solutions. A relation between these four pressures may readily be deduced from the three equilibrium equations

$$f_0(s, p, \theta) = f_0(s', p', \theta),$$

$$f_0(s, \Pi, \theta) = F_0(\Pi, \theta),$$

$$f_0(s', \Pi', \theta) = F_0(\Pi', \theta).$$

These three equations may be combined so as to form a single equation containing three potential differences, whose values, in terms of quantities which may be measured experimentally, are given by the equations

$$f_0(s, p, \theta) - f_0(s, \Pi, \theta) = (p - \Pi) P_0(s, \Pi \rightarrow p, \theta),$$

$$f_0(s', p', \theta) - f_0(s', \Pi', \theta) = (p' - \Pi') P_0(s', \Pi' \rightarrow p', \theta),$$

$$F_0(\Pi', \theta) - F_0(\Pi, \theta) = \int_{\Pi}^{\Pi'} V(x, \theta) dx.$$

On substituting these values in this equation we obtain the equation

$$\int_{\Pi}^{\Pi'} V(x, \theta) dx = (p - \Pi) P_0(s, \Pi \rightarrow p, \theta) - (p' - \Pi') P_0(s', \Pi' \rightarrow p', \theta). \quad \dots (9)$$

This equation (which, of course, is exact) may be regarded as the fundamental equation connecting the vapour-pressures of two solutions and the pressures under which they co-exist in osmotic equilibrium\*.

If we suppose that  $s > s'$ , then  $p > p'$ ; and rearranging the terms of the equation so as to involve directly the difference

\* If the concentration of one of the solutions is made equal to zero, and the two terms on the right-hand side of the equation are written in the form of definite integrals, we obtain Porter's result (*loc. cit.*) connecting the osmotic pressure and vapour-pressure of a solution.

of pressure  $p-p'$ , we obtain the equation

$$p-p' = \frac{\int_{\Pi}^{\Pi'} V(x, \theta) dx}{P_0(s, \Pi \rightarrow p, \theta)} + (p' - \Pi') \left\{ \frac{P_0(s', \Pi' \rightarrow p', \theta)}{P_0(s, \Pi \rightarrow p, \theta)} - 1 \right\} - (\Pi' - \Pi). \quad (10)$$

If we make  $s'=0$ , the osmotic difference of pressure becomes the so-called osmotic pressure of the solution and the equation becomes

$$\Omega(s, p_0, \theta) = \frac{\int_{\Pi}^{\Pi_0} V(x, \theta) dx}{P_0(s, \Pi \rightarrow p, \theta)} + (p_0 - \Pi_0) \left\{ \frac{v(0, \Pi_0 \rightarrow p_0, \theta)}{P_0(s, \Pi \rightarrow p, \theta)} - 1 \right\} - (\Pi_0 - \Pi). \quad (11)$$

This equation may be put into a form suitable for practical calculation by substitution of the values of  $P_0(s, \Pi \rightarrow p, \theta)$  and  $v(0, \Pi_0 \rightarrow p_0, \theta)$  given by equations (2) and (3). In this way we obtain the equation

$$\Omega(s, p_0, \theta) = \frac{\int_{\Pi}^{\Pi_0} V(x, \theta) dx}{P_0(s, \varpi, \theta)(1 - \lambda\epsilon)} + (p_0 - \Pi_0) \left\{ \frac{v(0, \varpi, \theta)(1 - \beta_0\epsilon_0)}{P_0(s, \varpi, \theta)(1 - \lambda\epsilon)} - 1 \right\} - (\Pi_0 - \Pi). \quad (12)$$

where

$$\epsilon = \frac{1}{2}(p + \Pi) - \varpi \text{ and } \epsilon_0 = \frac{1}{2}(p_0 + \Pi_0) - \varpi.$$

If we neglect the second and third terms and also the compressibility factor in the first term, we obtain an approximate value  $\Omega_a$  given by the equation

$$\Omega_a = \frac{\int_{\Pi}^{\Pi_0} V(x, \theta) dx}{P_0(s, \varpi, \theta)}.$$

In general it will be sufficiently accurate to calculate this value first, and then apply two corrections (1) a compressibility correction, equal to  $\Omega_a \lambda \{ \frac{1}{2}(p_0 + \Omega_a + \Pi) - \varpi \}$ , (2) a pure solvent pressure correction equal to the second term of the above expression with the compressibility factors omitted. Since the ratio of  $\Pi_0 - \Pi$  to  $\Omega$  is of the same order of magnitude as the ratio of the specific volume of the liquid to that of the vapour, the third term is negligible in all ordinary cases.

*The Comparison and Tabulation of Experimental Results.*

Vapour-pressure and osmotic pressure measurements form two independent methods of investigating the thermodynamical properties of solutions. The simplest method of comparing and tabulating such results is to calculate from the experimental data the lowering of the chemical potential of the solute at some standard pressure (atmospheric or the pure solvent vapour-pressure) \*. These calculations may be performed by means of equations (5) and (8). In the case of concentrated solutions it is impossible to measure the ordinary osmotic pressure. A possible way of carrying out the osmotic investigation of such solutions is to measure the equilibrium pressures of successive pairs of a series of solutions of gradually increasing concentration (starting from the pure solvent). If for example in each measurement the weaker solution was under atmospheric pressure, we should have

$$\begin{aligned} f_0(0, \varpi, \theta) - f_0(s_1, \varpi, \theta) &= \Omega_1 P_0(s_1, \varpi \rightarrow \varpi + \Omega_1, \theta), \\ f_0(s_1, \varpi, \theta) - f_0(s_2, \varpi, \theta) &= \Omega_2 P_0(s_2, \varpi \rightarrow \varpi + \Omega_2, \theta), \\ &\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ f_0(s_{n-1}, \varpi, \theta) - f_0(s_n, \varpi, \theta) &= \Omega_n P_0(s_n, \varpi \rightarrow \varpi + \Omega_n, \theta), \end{aligned}$$

where  $s_1, s_2, \dots, s_n$  are the successive values of the concentration and  $\Omega_1, \Omega_2, \dots, \Omega_n$  are the successive osmotic differences of pressure. The value of  $f_0(0, \varpi, \theta) - f_0(s_n, \varpi, \theta)$  may thus be found by adding the quantities on the right-hand sides of the above equations. It is perhaps hardly necessary to remark that the osmotic pressure of the strongest solution is not equal to the sum of the successive osmotic differences of pressure.

The University, Leeds,  
June 30th, 1911.

\* The fact that the thermodynamic potential is a more suitable magnitude to deal with than the osmotic pressure in the case of concentrated solutions, was pointed out by Duhem several years ago (*La Mécanique Chimique*, vol. iii. p. 70).

XCI. *Some Further Problems connected with the Motion of Charged Spheres.* By G. H. LIVENS, B.A., Fellow of Jesus College, Cambridge; Lecturer in Mathematics, Sheffield University\*.

# I. *The Vibration of a Charged Conducting Sphere.*

A GLANCE at the method previously employed to solve the case of the uniformly accelerated motion of the charged sphere, will suffice to show that it is merely the simplest of the soluble cases. In fact, the solution of the problem for any acceleration can be at once obtained, provided only that it is such that the displacement of the centre of the sphere in a time comparable with  $\frac{a}{c}$  is small compared with  $a$ . The solution for uniform motion was obtained by integrating the surface condition

$$a^2 f''(ct) + af'(ct) + f(ct) - e\xi = 0,$$

where  $\xi$  was taken to be  $\frac{1}{2}st^2$ . The solution consisted of a vibratory part not depending on  $\xi$  and the particular integral. In the general case

$$\xi = \int_0^t \int_0^t s \, dt \, dt,$$

and the success of the solution merely depends on being able to carry out these integrations and then in obtaining the particular integral of the above differential equation with the form of  $\xi$  thus obtained. As a case let us assume that

$$\xi = \frac{s}{n^2} \cos nt.$$

The particular integral is then easily seen to be

$$f(ct) = \frac{es}{c^2 n^2} \frac{\left(1 - \frac{a^2 n^2}{c^2}\right) \cos nt + \frac{an}{c} \sin nt}{\left(1 - \frac{a^2 n^2}{c^2}\right)^2 + \frac{a^2 n^2}{c^2}}.$$

The complementary integral representing the vibratory part of the solution will be exactly the same as before. If  $s$  is small enough the solution thus obtained will apply for any period of time, because the displacement of the sphere is always small. Thus the vibratory terms represented by the complementary function will ultimately decay and become

\* Communicated by the Author.

negligible and we can leave them out of the discussion. Thus the solution is obtained with

$$f(ct) = \frac{es}{c^2 n^2} \frac{\left(1 - \frac{a^2 n^2}{c^2}\right) \cos nt + \frac{an}{c} \sin nt}{1 - \frac{a^2 n^2}{c^2} + \frac{a^4 n^4}{c^4}}.$$

The density on the sphere is just as before

$$\sigma = \frac{1}{4\pi} \left( \frac{e}{a^2} - \frac{2f'' \cos \theta}{a} \right),$$

and the force on the sphere in the direction of motion is

$$P = \frac{2}{3} \frac{e}{a} f''(ct).$$

This gives

$$P = -\frac{2}{3} \frac{e^2}{ac^2} \frac{\left(1 - \frac{a^2 n^2}{c^2}\right) \cos nt + \frac{an}{c} \sin nt}{1 - \frac{a^2 n^2}{c^2} + \frac{a^4 n^4}{c^4}}.$$

This is the effective force resulting from the motion and is the force which would be required to produce it. The motion can be interpreted as a solution of the dynamical equation

$$m\ddot{\xi} + k\ddot{\xi} = P,$$

wherein

$$m = \frac{2}{3} \frac{e^2}{ac^2} \frac{\left(1 - \frac{a^2 n^2}{c^2}\right)}{\left(1 - \frac{a^2 n^2}{c^2}\right)^2 + \frac{a^2 n^2}{c^2}},$$

$$k = \frac{2}{3} \frac{e^2}{ac^2} \frac{\frac{an}{c} \cdot \frac{1}{n}}{\left(1 - \frac{a^2 n^2}{c^2}\right)^2 + \frac{a^2 n^2}{c^2}},$$

and  $P$  is the force above investigated. If  $\frac{na}{c}$  is small this is practically

$$m = \frac{2}{3} \frac{e^2}{ac^2},$$

$$k = \frac{2}{3} \frac{e^2}{c^3},$$



results which agree well with those obtained by Lorentz on more general grounds.

The mean rate of radiation calculated from the Poynting vector is easily seen to be

$$\frac{1}{3} \frac{e^2 s^2}{c^4 \left(1 - \frac{a^2 n^2}{c^2} + \frac{a^4 n^4}{c^4}\right)},$$

which agrees with Larmor's general result when  $\frac{an}{c}$  is small.

Walker works out the case of the sphere under the action of a given periodic force. The results can easily be deduced from those given above. Thus if we use

$$P = \lambda \cos nt,$$

then using the same  $m$  and  $k$  as before the solution for  $\xi$  is

$$\xi = \frac{\lambda}{2} \frac{e}{ac^2} \frac{\sqrt{1 - \frac{a^2 n^2}{c^2} + \frac{a^4 n^4}{c^4}}}{n^2} \cos (nt + \epsilon),$$

$$\text{where} \quad \tan \epsilon = \frac{\frac{an}{c}}{1 - \frac{a^2 n^2}{c^2}},$$

and the mean rate of radiation is

$$\frac{1}{3} \frac{e^2}{c^4} \cdot \frac{\lambda^2}{\left(\frac{2}{3} \frac{e^2}{ac^2}\right)^2} = \frac{3}{4} \frac{a^2 \lambda^2}{e^2}$$

and is independent of  $n$ .

## II. The Slow Rotation of Charged Spheres.

Walker works out first the case of the rotation of a perfectly conducting sphere rotating about a diameter. It is, however, difficult to imagine what the motion of the sphere has got to do with any motion of the electricity. The conductor, being perfect, is such that any charge on it is freely movable. A charge on a perfect conductor experiences no resistance to its motion due to the conductor. Thus for a slow rotation the motion of the conductor and the motion of the charge are independent of each other, and

the conditions of the one cannot be determined from those of the other.

The case of a dielectric is, however, different. The charge is here rigidly attached to the boundary and must move round if the sphere is rotated.

Adopting a similar notation to that employed in previous papers and following Walker's method closely, we assume the field to be of the form given by

$$X = \frac{e}{r^2}, \quad Y = 0, \quad Z = \frac{c \sin \theta}{r^2} (r^2 f'' + r f')$$

$$\alpha = \frac{2 \cos \theta}{r^3} (r f' + f), \quad \beta = \frac{\sin \theta}{r^3} (r^2 f'' + r f' + f), \quad \gamma = 0,$$

outside the sphere and inside

$$X = Y = 0, \quad Z = \frac{c' \sin \theta}{r^3} [r^2 (\phi_1'' + \phi_2'') + r (\phi_1' - \phi_2')],$$

$$\alpha = \frac{2 \cos \theta}{r^3} [r (\phi_1' - \phi_2') + \phi_1 + \phi_2],$$

$$\beta = \frac{\sin \theta}{r^3} [r^2 (\phi_1'' + \phi_2'') + r (\phi_1' - \phi_2') + \phi_1 + \phi_2].$$

$f$  is a function of  $(ct - r)$ ,  $\phi_1$  of  $(c't - r)$  and  $\phi_2$  of  $(c't + r)$ , all being supposed to be small quantities proportional to the angular velocity  $\omega$ , and squares of  $\omega$  are neglected.

Since the field must be finite at the origin we must have

$$\phi_1(c't) + \phi_2(c't) = 0. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The normal component of the magnetic force is continuous at  $r = a$ . Thus

$$a f' + f = a (\phi_1' - \phi_1'') + \phi_1 + \phi_2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and this, according to Walker, also secures the continuity of the tangential component of electric force at  $r = a$ .

The discontinuity of the tangential component of the magnetic force determines the surface current which is due to the rotation of the uniform surface charge  $\sigma = \frac{e}{4\pi a^2}$  rotating with the sphere. Thus if  $\omega$  is the angular velocity of the sphere, supposed to be rotating round the polar axis, we have

$$\frac{ea^2\omega}{c^2} = a^2 f'' + a f' + f - [a^2 (\phi_1'' + \phi_2'') + a (\phi_1 - \phi_2') + \phi_1 + \phi_2],$$

or using the relation (2) above

$$\frac{e\omega}{c^2} = f'' - \phi_1'' - \phi_2''.$$

The tangential component of the electric force is

$$Z = -\frac{c \sin \theta}{a^2} (af'' + f')$$

and the total couple on the sphere is

$$\int \sigma Z a \sin \theta ds = -\frac{2}{3} \frac{ec}{a} (af'' + f').$$

These results are quite general. Now let us try a solution of the conditions when the sphere has a uniform angular acceleration round the axis equal to  $\dot{\omega}$ . The conditions to determine  $f$ ,  $\phi_1$  and  $\phi_2$  are then

$$af' + f = a(\phi_1' - \phi_2') + \phi_1 + \phi_2$$

$$f'' - \phi_1'' - \phi_2'' = \frac{e\dot{\omega}t}{c}.$$

The particular solution of these conditions is found to be

$$f(ct-r) = \frac{1}{3} \frac{ea^2\dot{\omega}}{c^3} (ct-r),$$

$$\phi_1(c't-r) = \frac{1}{48} \frac{e\dot{\omega}K^{\frac{1}{2}}}{ac^3} (c't-r)^4,$$

$$\phi_2(c't+r) = -\frac{1}{48} \frac{e\dot{\omega}K^{\frac{1}{2}}}{ac^3} (c't+r).$$

where  $K = \frac{c^2}{c'^2}$  is the specific inductive capacity of the sphere.

In addition to this particular solution we have an oscillatory part represented by the complementary integral of the conditions. This is obtained by trying solutions of the conditions with  $\dot{\omega}=0$  of the form

$$f(ct-r) = Ae^{\lambda\left(\frac{ct-r+a}{a}\right)},$$

$$\phi_1(c't-r) = Be^{\lambda'\left(\frac{c't-r}{a}\right)},$$

$$\phi_2(c't+r) = -Be^{\lambda'\left(\frac{c't+r}{a}\right)},$$

which satisfy all the conditions if  $\lambda c = \lambda' c'$  and also

$$A(\lambda + 1) = B[(\lambda' + 1)e^{-\lambda'} + (\lambda' - 1)e^{\lambda'}],$$

$$A\lambda^2 = B\lambda'^2[e^{-\lambda'} - e^{\lambda'}],$$

which leads to a period equation for  $\lambda$  of the form

$$\tanh K^{\frac{1}{2}}\lambda = \frac{K^{\frac{1}{2}}\lambda}{K\lambda + K - 1}.$$

This equation has only one real root, a negative one whose numerical value is less than  $K^{-\frac{1}{2}}$  and which therefore becomes very small if  $K$  is large. All the other roots are complex and represent oscillations in the field.

The problem has therefore been completely determined as far as we are able to go. If we assume that the damped oscillations represented by the complementary integral of the conditions become evanescent before the solution here given ceases to hold, we can go one step farther.

Neglecting these oscillations, the couple necessary to keep the sphere going is

$$\begin{aligned} & -\frac{2}{3} \frac{ec}{a} \cdot \frac{1}{3} \frac{ea^2\dot{\omega}}{c^3} \\ & = -\frac{2}{9} \frac{e^2a\dot{\omega}}{c^2}, \end{aligned}$$

and this determines the effective inertia to the motion which arises from the electric charge.

This paper concludes my immediate object of interpreting the principal results of Walker's paper without any of the complications caused by introducing the material mass of the sphere. The results are all capable of a reasonable interpretation without this complication and they then lend their support to the idea of a purely electromagnetic constitution of the electron.

Sheffield, May 1911.

XCII. *On the Periodic Times of Saturn's Rings.*

By HENRY WILDE, D.Sc., D.C.L., F.R.S.\*

IN my paper on the "Origin of Cometary Bodies and Saturn's Rings," read before the Society in October last † a new determination was made of the periodic times of the rings, based on the commonly accepted distance of Mimas, 3·36 Saturnian units. This element of the orbit was derived from observations made by Herschel and subsequently adopted by all astronomical writers.

Recent observations of American astronomers with more powerful telescopes and under more favourable conditions, have reduced the distance of Mimas from the planet to 3·16 units, with the consequent increase in the times of rotation of the rings.

The difference between the older and later determinations is sufficiently large to induce me to place on record for comparison the results computed from both observations and Kepler's third law, as shown and demonstrated in the following tables:—

Distances of Mimas = 3·36 and outer edge of ring A = 2·3.

$$(1) 3 \cdot 36^3 : 2 \cdot 3^3 :: 22\text{h. } 37^2\text{m.} : x = 12\text{h. } 48^2\text{m. for A.}$$

Distances of Mimas = 3·36 and inner edge of ring C = 1·27.

$$(2) 3 \cdot 36^3 : 1 \cdot 27^3 :: 22\text{h. } 37^2\text{m.} : x = 5\text{h. } 15^2\text{m. for C.}$$

Distances of Mimas = 3·16 and outer edge of ring A = 2·3.

$$(3) 3 \cdot 16^3 : 2 \cdot 3^3 :: 22\text{h. } 37^2\text{m.} : x = 14\text{h. } 4^2\text{m. for A.}$$

Distances of Mimas = 3·16 and inner edge of ring C = 1·27.

$$(4) 3 \cdot 16^3 : 1 \cdot 27^3 :: 22\text{h. } 37^2\text{m.} : x = 5\text{h. } 45^2\text{m. for C.}$$

The unit distance, 3·16, for Mimas necessarily involves the correlative reduction of the distances of the other Saturnian satellites, as now set forth in the tables of these elements published by American astronomers.

That Saturn's rings are ejectamenta from the interior of the planet is further evident from the fact that no causal connexion subsists between their times of rotation and that of the planet itself, as the inner edge of the ring C has a

\* Communicated by the Author. From the Manchester Memoirs, vol. lv. 1910–11, no. 14.

† Manchester Memoirs, vol. lv. 1910–11; Phil. Mag. November 1911.  
Phil. Mag. S. 6. Vol. 22. No. 132. Dec. 1911. 3 R

periodic time of only 5 hours 45 minutes, while the axial rotation of Saturn is 10 hours 13 minutes.

The same conclusion may also be drawn with reference to the origin of the two satellites of Mars, as Phobos has a period of only 7 hours 39 minutes, while the axial rotation of the planet is 24 hours 37 minutes.

The comparative minuteness of these bodies, which are estimated to be less than 10 miles in diameter, indicates them as ejectamenta rather than the successive condensations of a nebular substance surrounding the planet.

Saturn's dusky ring and the inner satellite of Mars are the only bodies in the solar system that revolve in a shorter time than their primaries.

#### ELEMENTS OF SATURN'S RINGS.

$$\text{Mimas} = 3.16.$$

Rings.	Distance from centre of Saturn.		Time of Revolution.	
	Sat. Units.	Miles.	h.	m.
Exterior A .....	2.30	84,937	14	4
Breadth .....	0.26	9,602	"	"
Mid-breadth .....	2.17	80,138	12	51
Interior A .....	2.04	75,337	11	44
Interval .....	0.07	2,585	"	"
Exterior B .....	1.97	72,752	11	8
Breadth .....	0.47	17,357	"	"
Mid-breadth .....	1.735	64,073	9	12
Interior B .....	1.50	55,395	7	23
Exterior C .....	1.50	55,395	7	23
Breadth .....	0.23	8,493	"	"
Mid-breadth .....	1.385	51,148	6	33
Interior C .....	1.27	46,901	5	45
Ball Space .....	0.27	9,971	"	"
Sat. Ball .....	1.00	36,930	10	13
Mimas .....	3.16	116,698	22	37

XCIII. *Notices respecting New Books.*

*A History of the Theories of Æther and Electricity from the Age of Descartes to the close of the Nineteenth Century.* By E. T. WHITTAKER, *Sc.D., F.R.S.* Pp. xv + 475. London: Longmans, Green & Co. Dublin: Hodges, Figgis & Co., 1910. Price 12s. 6d. nett.

IT is not often that an historian exhibits an equal insight into his subject to that which Dr. Whittaker shows in this remarkable work. In reading it one is over and over again struck with wonder at how he has found time in the midst of his other duties even to collate the vast amount of material which the book contains. But it is not a mere collection. Each stage in discovery is subjected to a clear criticism which places it accurately in relation to preceding and subsequent discoveries. The whole must have involved a most painstaking examination of even out-of-the-way and little known theories over which "the iniquity of oblivion has scattered everywhere her poppy." The result is a volume which will be of immense value to the physicist in giving him a clear conception of the nature of the gradual advance which has taken place from the time of Descartes onwards. It may be divided roughly into two portions, viz., that dealing with light, and that dealing with electricity: these, of course, run side by side and ultimately coalesce into one subject. One important point in the treatment is that in the presentation of the mathematical development, the notation and method of proof are in every case modernised so that they become immediately intelligible. This is done without sacrificing in any way the original character of the argument, so that nothing essential is lost and much is gained in the way of lucidity. As an illustration of the exhaustive way in which Dr. Whittaker deals with a subject, take the case of the pressure of light. On this subject "an experiment was performed in 1708 by Homberg, who imagined that he actually obtained the effect in question; but Mairan and Du Fay in the middle of the century, having repeated his operations, failed to confirm his conclusion." "The subject was afterwards taken up by Michell, who 'some years ago,' wrote Priestley in 1772, 'endeavoured to ascertain the momentum of light in a much more accurate manner. . . . He exposed a very thin and delicately-suspended copper plate to the rays of the sun concentrated by a mirror and observed a deflexion. . . .' A similar experiment was made by A. Bennet [the inventor of the gold-leaf electroscope] who directed the light from the focus of a large lens on writing paper delicately suspended in an exhausted receiver 'but could not perceive any motion distinguishable from the effects of heat.' These experiments were made of course in connexion with the corpuscular theory, and Bennet concluded from his negative result that "heat and light may not be caused by the influx or rectilineal projections of fine particles but by the vibrations made in the universally diffused *caloric* or matter of

heat or fluid of light." Young came to the same conclusion. "But Euler many years before had expressed the opinion that light-pressure might be just as reasonably expected on the undulatory as on the corpuscular theory." "Euler . . . . accounted for the tails of comets by supposing that the solar rays, impinging on the atmosphere of a comet, drive off from it the more subtle of its particles." Then follows a full exposition of the contributions of Maxwell, Bartoli, Boltzmann, and a reference to Lebedew's earlier work. The full experimental verification, of course, belongs to the twentieth century.

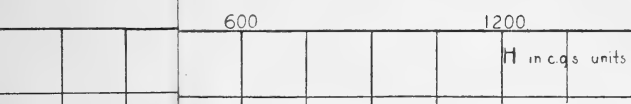
The most interesting and certainly the most important part of this history deals with the development of electrical theory from the time of Maxwell onwards. Maxwell had added a displacement current to the conduction current; FitzGerald added the convection current,  $\rho W$ ; Hertz and Heaviside showed that in the case of moving media the term curl ( $D.W$ ) must, in accordance with their conceptions, be added in order to obtain the total current—*i. e.*, that a dielectric which moves in an electric field is the seat of an electric current which produces a magnetic field in the surrounding space. Later on, Lorentz replaced this last term by curl ( $P.W$ ) which implies that the moving dielectric does not carry on the æthereal displacement but only carries along the charges which exist at opposite ends of the molecules of the ponderable dielectric and which are represented by  $P$ , the polarization. The subject is too complicated and the different issues that arise far too numerous to be summarised here; but Dr. Whittaker leads the reader on from point to point till (at any rate if he has been long enough acquainted with the subject) he seems to live over again the developments that have taken place but with the fuller understanding which the author's critical acumen imparts.

The book is excellently edited. We notice 'conduction' instead of 'convection' on p. 367 (beneath the first formula). The use of an unmistakable small numeral one to stand for current looks very odd in formulæ; it has apparently been adopted because the dot of a small  $i$  would be mistakable for time-differentiation since the fluxional notation is commonly adopted. Perhaps the name of the eldest Becquerel should have been mentioned in connexion with the earliest experimental work in thermoelectricity. Poincaré's criticism of Maxwell's stresses probably does not come within the time-range of the book but might perhaps be alluded to in a footnote. The present writer has endeavoured to recall the early work on those parts of the subject with which he is most familiar; but in each case on turning up here he has found at least as much as he had re-collected.

It should be added that the book is not intended for an elementary student. A man will require some considerable general knowledge before he will be able satisfactorily to tackle it; but to the properly equipped man it is a mine of erudition and carefully reasoned criticism.



FIG. 9.



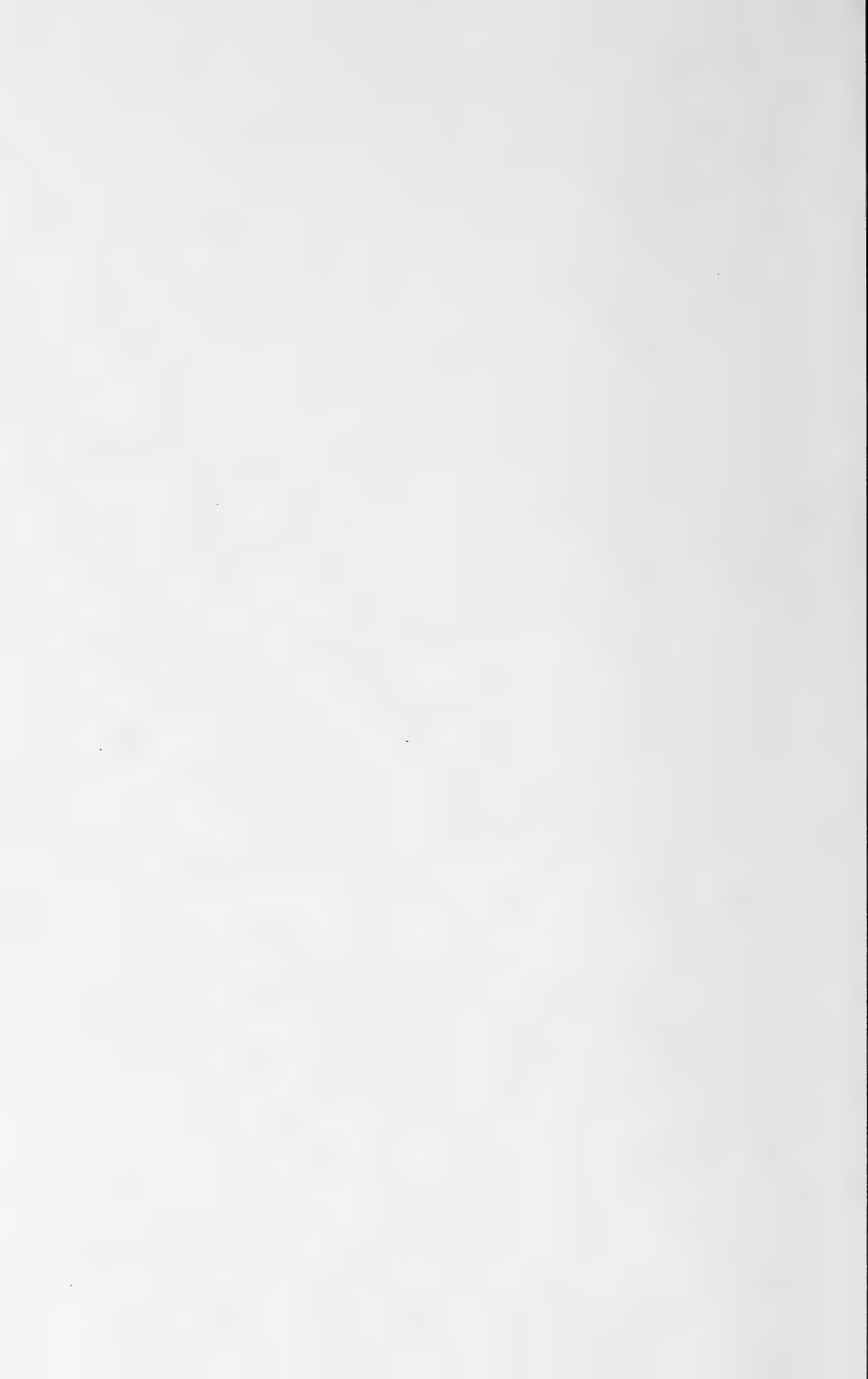
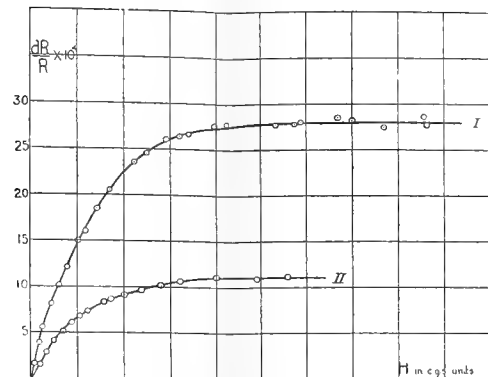
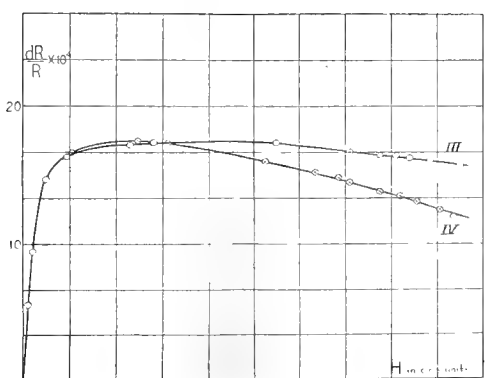


FIG. 1.



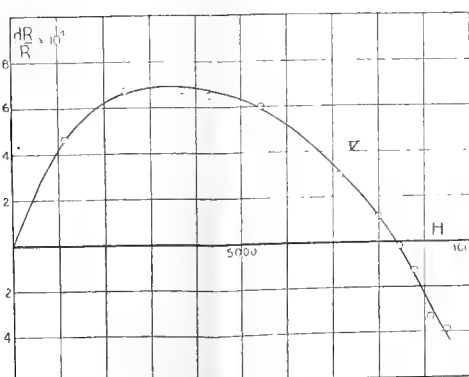
IRON

FIG. 2.



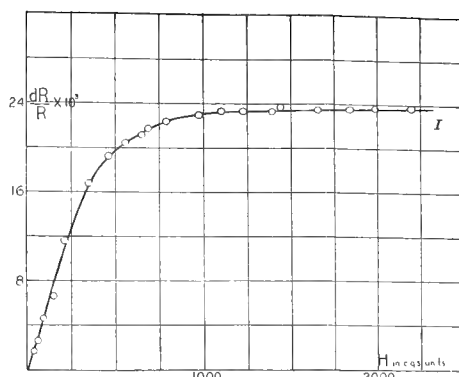
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FIG. 3.



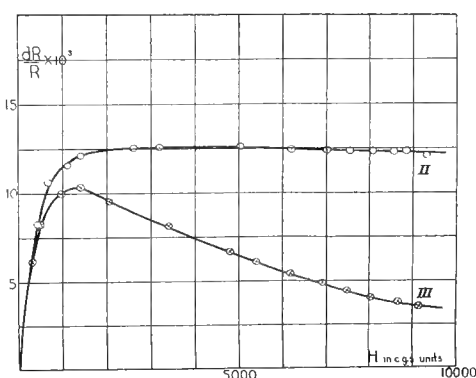
IRON

FIG. 4.



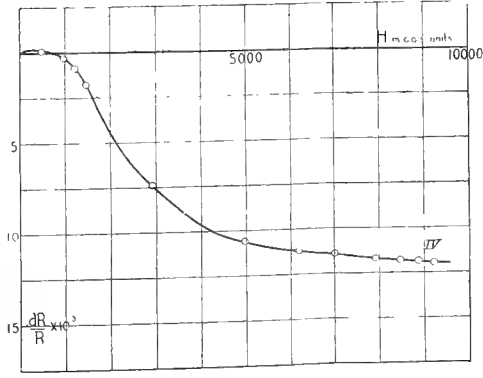
NICKEL

FIG. 5.



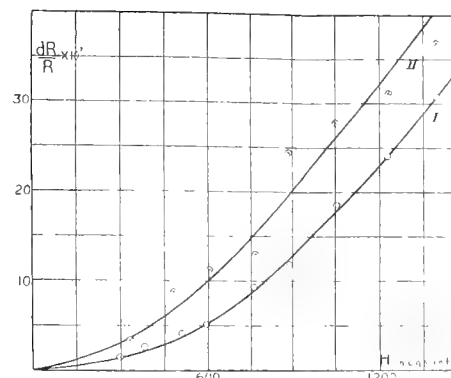
NICKEL

FIG. 6.



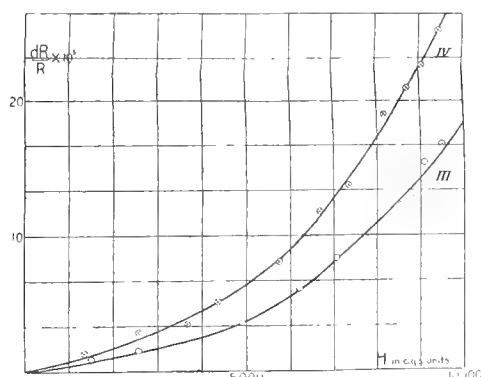
NICKEL

FIG. 7.



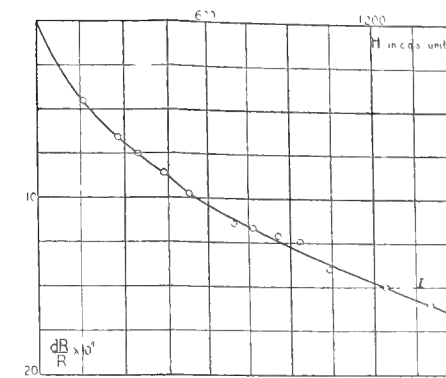
CADMIUM

FIG. 8.



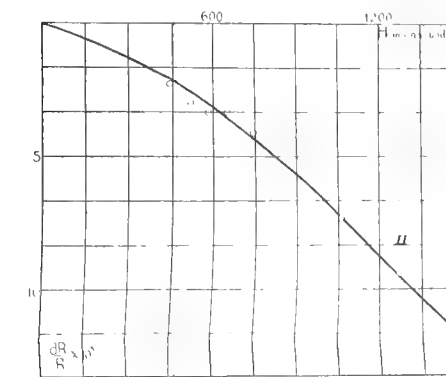
CADMIUM

FIG. 9.



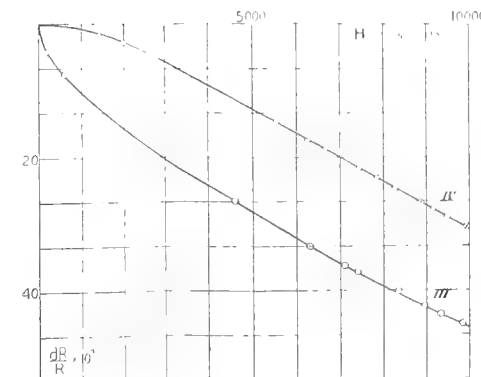
HEUSLER ALLOY

FIG. 10.



HEUSLER ALLOY

FIG. 11.



HEUSLER ALLOY

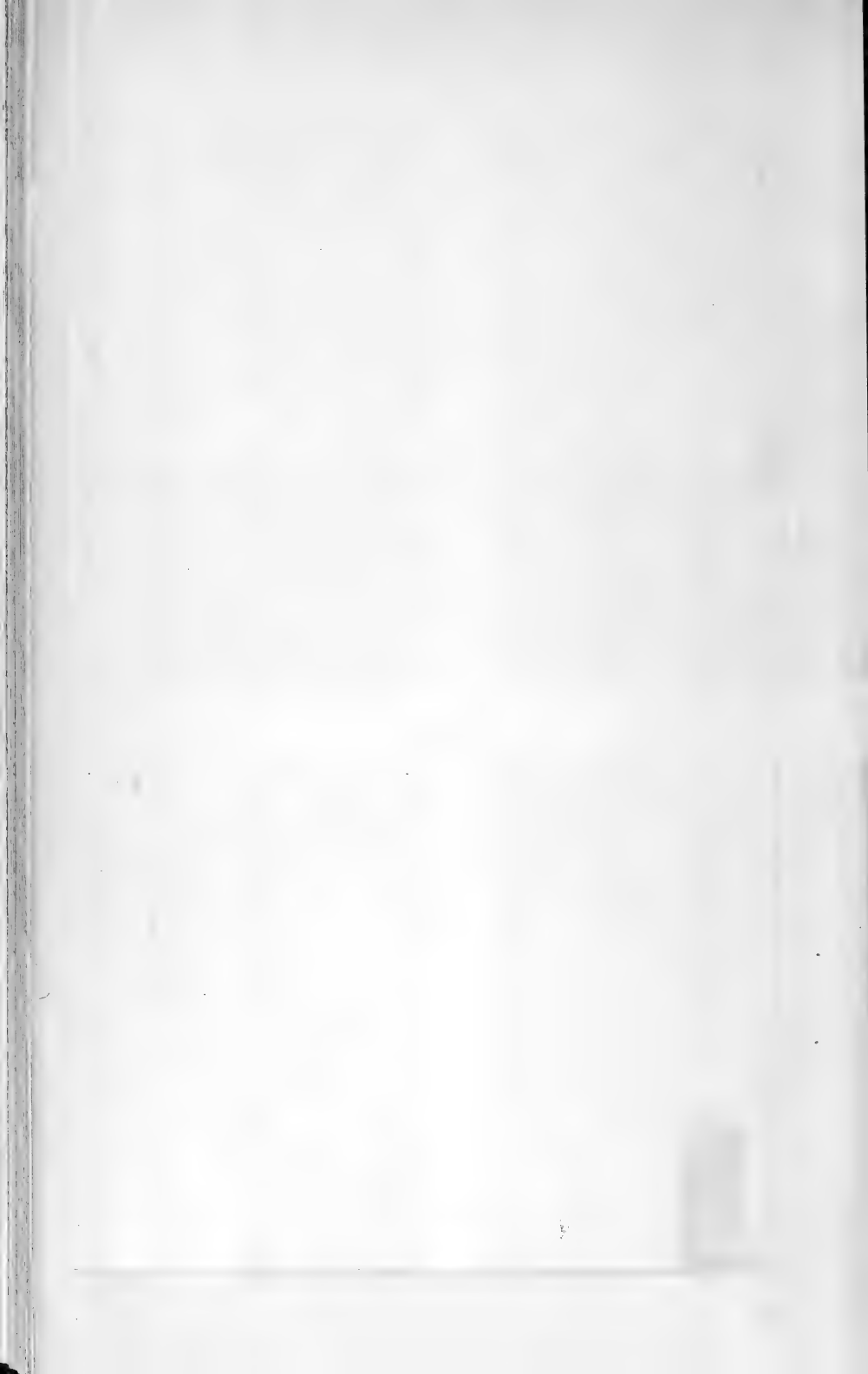


FIG. 2.



FIG. 3.



FIG. 4.



FIG. 5.





XCIV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 820.]

May 24th, 1911.—Prof. W. W. Watts, Sc.D., M.Sc., F.R.S.,  
President, in the Chair.

THE following communication was read:—

‘On the Geology of Antigua and other West Indian Islands, with Reference to the Physical History of the Caribbean Region.’  
By R. J. Lechmere Guppy.

After noticing the work of former observers on the geology of Antigua, the author gives a brief description of the formations of that island, showing that it is divided into three principal regions—(1) the Volcanic (or Igneous) Region; (2) the Central Plain; and (3) the Calcareous Formation: the first-named being, according to previous authors, the oldest, as it is pre-Tertiary, and the others following in succession. The Calcareous Formation, hitherto considered the newest, contains fossils, of which the most remarkable is a species of *Orbitoides*. After a discussion of these formations, and especially of the evidence for the so-called ‘Oligocene’ age of the Calcareous Formation, the conclusion is reached that this formation is the oldest—not the youngest, and is probably Eocene or older. The island was raised above sea-level by the development of the great Antillian dislocation, which is described, and divides each of the islands of Guadeloupe and Antigua into two parts, of which the eastern is calcareous and the western volcanic. In Antigua the Central Plain intervenes between the two parts, while in Guadeloupe they are only separated by a narrow channel. In support of this proposition the physical features of Antigua are discussed, and it is shown that the island has not been submerged since the volcanic period.

The position and age of the Scotland Series of Barbados are then discussed, and that Series is shown to be Eocene, the lower beds being possibly Cretaceous and being a remnant of the Atlantis Continent.

The extension, age, and position of the *Orbitoides* Bed of Trinidad are next dealt with, and some further remarks are added on the physical history of the Caribbean Region.

## INDEX to VOL. XXII.

- ABERRATION** in a dispersive medium, on, 130.
- Absorption and dispersion, on, 303.
- Acceleration, on the direction of, 458.
- Actinium emanation, on the transformation of the, 201.
- Adams (Prof. E. P.) on electrostriction, 889.
- Air, on the coefficient of absorption by, of the beta rays from radium C, 8; on the production of nuclei in, by intense cooling, 563.
- Airey (J. R.), tables of Neumann functions, 658.
- Alpha particles, on the probability variations in distribution of, 198; on the ranges of the, from various radioactive substances, 613.
- rays, on the emission of electrons from metals under the influence of, 907.
- Aluminium phosphate, on the positive ionization from, 698; on the mobility of positive ions from heated, 791.
- Antonoff (G. N.) on the disintegration products of uranium, 419.
- Arnold (H. D.) on Stokes's law for the motion of spheres through liquids, 755.
- Atmosphere, on the amount of the radioactive products present in the, 821.
- Atomic volume, on the relation between the, and the spectra of elements, 922.
- Barkla (Prof. C. G.) on the spectra of the fluorescent Röntgen radiations, 396.
- Barus (Prof. C.) on elliptic and other interference with reflecting gratings, 118.
- Batschinski (A.) on the equation of continuity of the liquid and gaseous states of matter, 221.
- Becker (G. F.) on some new mechanical quadratures, 342.
- Berkeley (the Earl of) on a thermostat for controlling the temperature of a room, 211.
- Berry (G. H.) on the pianoforte bridges, 113.
- Beryllium, on the positive ionization from salts of, 669.
- Beta particles, on the relative number of ions produced by the, from the various radioactive substances, 604.
- rays, on the coefficient of absorption by air of the, from radium C, 8; on the number of ions produced by the, from radium C, 551.
- Bifilar suspensions, on increased accuracy in the use of, 433.
- Bois (Prof. H. du) on polarization of undiffracted long-waved heat rings by wire gratings, 322.
- Boltwood (Prof. B. B.) on the production of helium by radium, 586.
- Books, new:—U.S. Coast and Geodetic Survey, 219, 355; Bulletin of the Bureau of Standards, 354; Fleming's Principles of Electric Wave Telegraphy and Telephony, 463; Gesammelte Abhandlungen von Friedrich Kohlrausch, 819; Walker's Outlines of the Theory of Electromagnetism, 819; Whitaker's History of the Theories of Æther and Electricity, 951.
- Boyle (Dr. R. W.) on the solubility of radium emanation, 840.
- Bragg (Prof. W. H.) on the mode of ionization by X-rays, 222.
- Bridges, on the pianoforte, 113.
- Bumstead (Prof. H. A.) on the emission of electrons by metals under the influence of alpha rays, 907.



- Burton (Dr. C. V.) on a thermostat for controlling the temperature of a room, 211.
- Calcium nitrate, on the positive ionization from, 672.
- Campbell (N.) on delta rays, 276.
- Carter (H.) on the radioactive properties of high temperature flames, 805.
- Cathode rays, on the variation of ionizing power with the velocity of, 647.
- Chemical elements, on a structural theory of the, 864.
- potential, on the application of the theory of, to the thermodynamical theory of solutions, 933.
- Chladni's figures, on the calculation of, for a square plate, 225.
- Cometary bodies, on the origin of, 741.
- Condenser, on the magnetic field produced by a charged, moving through space, 150.
- Conduction, on the mode of, in gases, 1, 656, 816; on the number of electrons concerned in metallic, 245; problems in the, of heat, 381.
- Constants, Annual Tables of, 223.
- Continuity of the liquid and gaseous states, on the equation of, 221.
- Crandall (I. B.) on groove-form and energy distribution of diffraction gratings, 534.
- Delta rays, on, 276.
- Dielectric sphere, on the initial accelerated motion of a rigidly charged, 169.
- Diffraction gratings, on groove-form and energy distribution of, 534.
- Dispersion, on absorption and, 363.
- Dispersive medium, on aberration in a, 130.
- Ditto (R. C.) on the diffusion of neon through hot quartz, 704.
- Donaldson (H.) on the spectra of the electrodeless ring discharge in certain gases, 720.
- Earth, on the age of the, 357; on the rigidity of the, 481; on the intensity of the penetrating radiation of the, at different altitudes, 639.
- Electric discharge, on the intensity of the ultra-violet light emitted by an, at low pressures, 412.
- Electric experiments with mercury contained in tubes, on, 506.
- vacuum valves, on the mode of conduction in gases illustrated by the behaviour of, 1.
- Electricity, on rays of positive, from the Wehnelt cathode, 926.
- Electrolytes, on weak, and a dynamical theory of solutions, 17.
- Electrons, on the emission and absorption of energy by, 66; on the number of, concerned in metallic conduction, 245; on the emission of, by metals under the influence of alpha rays, 907.
- Electrostriction, on, 889.
- Elements, on a structural theory of the, 864; on a relation between the atomic volumes and spectra of the, 992.
- Elliptic interference with reflecting gratings, on, 118.
- Emanation, on the solubility of radium, 840.
- Emanations, on the transformation and nomenclature of the, 621.
- Energy, on the emission and absorption of, by electrons, 66; on the problem of partition of, 663.
- Equation, on Fourier's theorem concerning the roots of an algebraical, 173, 668.
- Eve (Dr. A. S.) on the coefficient of absorption by air of the beta rays from radium C, 8; on the number of ions produced by the beta rays and by the gamma rays from radium C, 551.
- Fajans (Dr. K.) on radioactive products of short life, 629.
- Falconer (Dr. J. D.) on the geology of Northern Nigeria, 820.
- Flames, on the mobility of the positive ion in, 775; on the radioactive properties of high temperature, 805.
- Force, on the direction of, 458.
- Fourier's theorem concerning the roots of an algebraical equation, on, 173, 668.
- Franck (Dr. J.) on the question of valency in gaseous ionization, 547.
- Fresnel's theory of the reflexion of light, on some consequences of, 305.

- Gamma rays, on the number of ions produced by the, from radium C, 551.
- Gaseous ionization, on the question of valency in, 547.
- Gases, on the mode of conduction in, 1, 656, 816; on the charges on ions in, 204; on the spectra of the electrodeless ring discharge in certain, 720; on the separation of spectra in compound, 727; on the mobility of positive ions from heated aluminium phosphate in, at low pressures, 791.
- Geiger (Dr. H.) on the transformation of the actinium emanation, 201; on the relative number of ions produced by the  $\beta$  rays from the various radioactive substances, 604; on the ranges of the  $\alpha$  particles from the radioactive substances and a relation between range and period of transformation, 613; on the transformation and nomenclature of the radioactive emanations, 621.
- Geological Society, proceedings of the, 220, 465, 820, 953.
- Gill (E. W. B.) on the intensity of the ultra-violet light emitted by an electrical discharge at low pressures, 412.
- Glasson (J. L.) on the variation of ionizing power with the velocity of cathode rays, 647.
- Gradation, on the enhancing of photographic, 734.
- Gratings, on elliptic and other interference with reflecting, 118; on polarization of undiffracted long-waved heat rays by wire, 322; on groove-form and energy distribution of diffraction, 554.
- Groove-form and energy distribution of diffraction gratings, on, 534.
- Guppy (R. J. L.) on the geology of Antigua, 953.
- Gwyther (R. F.) on the stresses in a heavy spherical shell, 191.
- Heaps (C. W.) on the effect of magnetic fields on metallic resistance, 900.
- Heat, on problems in the conduction of, 381.
- rays, on polarization of undiffracted long-waved, by wire gratings, 322.
- Helium, on the production of, by radium, 586.
- group of gases, on the resonance spectra of iodine vapour and their destruction by the, 469.
- Horton (Dr. F.) on the origin of spectra, 214.
- Houstoun (Dr. R. A.) on a relation between tension and torsion, 740.
- Induction-coil, on the, 706.
- Interference, on elliptic and other, with reflecting gratings, 118.
- Iodine vapour, on the resonance spectra of, 469.
- Ionization, on the mode of, by X-rays, 222; on the question of valency in gaseous, 547; on the positive, from hot salts, 669.
- Ionizing power, on the variation of, with the velocity of cathode rays, 647.
- Ions, on charges on, in gases, 204; on the number of, produced by the beta rays and by the gamma rays from radium C, 551; on the relative number of, produced by the  $\beta$  particles from the various radioactive substances, 604; on the mobility of the positive, in flames, 775; on the mobility of positive, produced from heated aluminium phosphate in gases at low pressures, 791.
- Joly (Prof. J.) on a method of investigating the quantity of radium in rocks and minerals, 134; on the age of the earth, 357.
- Jones (Prof. E. T.) on the induction-coil, 706.
- Kinoshita (S.) on the amount of the radioactive products present in the atmosphere, 821.
- Kleeman (Dr. R. D.) on the laws of molecular attraction, 355; on molecular attraction and the properties of liquids, 566.
- Knipp (Prof. C. T.) on rays of positive electricity from the Wehnelt cathode, 926.
- Kovarik (Dr. A. F.) on the relative number of ions produced by the  $\beta$  particles from the various radioactive substances, 604.
- Lémeray, (E. M.) on the principle of relativity, 222.

- Lewis (Dr. W. C. McC.) on the internal pressure of a liquid, 193; on the latent heat of vaporization of liquids, 268.
- Light, on the reflexion of, at certain metal-liquid surfaces, 229; on some consequences of Fresnel's theory of the reflexion of, 305; on the intensity of the ultra-violet, emitted by an electrical discharge at low pressures, 412; on the difference in the photoelectric effect caused by incident and emergent, 854.
- Lines of force due to given static charges, on, 177.
- Liquid, on the internal pressure of a, 193; on the reflexion of light at metal-, surfaces, 229.
- Liquid and gaseous states of matter, on the continuity of the, 221.
- Liquids, on the latent heat of vaporization of, 268; on molecular attraction and the properties of, 566; on limitations imposed by slip and inertia terms upon Stokes's law for the motion of spheres through, 755.
- Livens (G. H.) on the initial accelerated motion of a rigidly charged dielectric sphere, 169; on further problems in the motion of charged spheres, 943.
- Lodge (Sir Oliver) on the mode of conduction in gases illustrated by the behaviour of electric vacuum valves, 1, 656.
- Lotka (A. J.) on the ratios which the amounts of substances in radioactive equilibrium bear to one another, 353.
- Lusby (S. G.) on the mobility of the positive ion in flames, 775.
- Macallum (E. N.) on the intensity of the earth's penetrating radiation at different altitudes and a secondary radiation excited by it, 639.
- McLaren (S. B.) on the emission and absorption of energy by electrons, 66.
- McLennan (Prof. J. C.) on the intensity of the earth's penetrating radiation at different altitudes and a secondary radiation excited by it, 639.
- Magnetic fields produced by charged condensers moving through space, on the, 150; on the effect of, on metallic resistance, 900.
- Mallik (Prof. D. N.) on lines of force due to given static charges, 177.
- Manlove (L. R.) on a proposed method for the better practical application of Fourier's theorem concerning the roots of an algebraical equation, 173, 668.
- Mechanics, on non-Newtonian, 458.
- Mercury, on electrical experiments with, contained in tubes, 506.
- Metal-liquid surfaces, on the reflexion of light at, 229.
- Metallic conduction, on the number of ions concerned in, 245.
- resistance, on the effect of magnetic fields on, 900.
- Metals, on the optical properties of fused, 266; on the emission of electrons by, under the influence of alpha rays, 907.
- Mills (Dr. J. E.) on the relation of temperature and molecular attraction, 84.
- Minerals, on a method of investigating the quantity of radium in, 134.
- Molecular attraction, on the relation of temperature and, 84; on the laws of, 355; on, and the properties of liquids, 566.
- Moseley (H. G. J.) on radioactive products of short life, 629.
- Neon, on the diffusion of, through hot quartz, 704.
- Neumann functions, tables of, 658.
- Nicholson (Dr. J. W.) on the number of electrons concerned in metallic conduction, 245; on the optical properties of fused metals, 266; on a structural theory of the chemical elements, 864.
- Nishikawa (S.) on the amount of the radioactive products present in the atmosphere, 821.
- Non-Newtonian mechanics, on, 458.
- Nuclei, on the production of, in air by intense cooling, 563.
- Nuttall (J. M.) on the ranges of the  $\alpha$  particles from various radioactive substances and a relation between range and period of transformation, 613.

- Ono (S.) on the amount of the radioactive products present in the atmosphere, 821.
- Optical properties of fused metals, on the, 266.
- Osmotic pressure and vapour pressure of solutions, on, 933.
- Owen (Dr. G.) on the production of nuclei in air by intense cooling, 563.
- Peddie (Prof. W.) on the problem of partition of energy, especially in radiation, 663.
- Photoelectric effect, on the difference in the, caused by incident and emergent light, 854.
- Photographic reproduction, on the general problem of, 734.
- Pianoforte bridges, on the, 113.
- Plate, on the calculation of Chladni's figures for a square, 225.
- Polarization of undiffracted long-waved heat rays by wire gratings, on, 322.
- Positive electricity, on rays of, from the Wehnelt cathode, 926.
- ionization from hot salts, on the, 669.
- Prescott (J.) on the rigidity of the earth, 481.
- Pressure, on the internal, of a liquid, 193.
- Probability variations in the distribution of  $\alpha$  particles, on the, 198.
- Quadratures, on some new mechanical, 342.
- Quartz, on the phosphorescence of fused, 533; on the diffusion of neon through hot, 704.
- Radiation, on the intensity of the earth's penetrating, at different altitudes, 639.
- Radioactive emanations, on the transformation and nomenclature of the, 621.
- equilibrium, on the ratios of substances in, 353.
- products of short life, on, 629; on the amount of the, present in the atmosphere, 821.
- properties of high temperature flames, on the, 805.
- substances, on the relative number of ions produced by the  $\beta$  particles from the various, 604; on the ranges of the  $\alpha$  particles from various, 613.
- Radioactivity, on the calculation of the age of the earth by, 370.
- Radium, on a method of investigating the quantity of, in rocks and minerals, 134; on the production of helium by, 586.
- B, on the relative number of ions produced by the  $\beta$  particles from, 604.
- C, on the coefficient of absorption by air of the beta rays from, 8; on the number of ions produced by the beta rays and by the gamma rays from, 551; on the relative number of ions produced by the  $\beta$  particles from, 604.
- emanation, on the solubility of, 840.
- Rastall (R. H.) on the geology of the districts of Worcester, Robertson, and Ashton, 466.
- Rayleigh (Lord) on aberration in a dispersive medium, 130; on the calculation of Chladni's figures for a square plate, 225; problems in the conduction of heat, 381; on the general problem of photographic reproduction, with suggestions for enhancing gradation originally invisible, 734.
- Reflexion of light, on the, at metal-liquid surfaces, 229; on some consequences of Fresnel's theory of the, 305.
- Relativity, on the principle of, 222.
- Resistance, on the effect of magnetic fields on metallic, 900.
- Resonance spectra of iodine vapour, on the, 469.
- Richardson (Prof. O. W.) on the positive ionization from hot salts, 669; on the diffusion of neon through hot quartz, 704.
- Rigidity of the earth, on the, 481.
- Ring discharge, on the spectra of the electrodeless, in certain gases, 720.
- Roberts (D. E.) on the induction-coil, 706.
- Rocks, on a method of investigating the quantity of radium in, 134.
- Röntgen radiation, on the spectra of fluorescent, 396; on the transformation of the energy of homogeneous, into energy of corpuscular radiation, 447.

- Rossi (R.) on a relation between the atomic volumes and the spectra of elements, 922.
- Rubens (Prof. H.) on polarization of undiffracted long-waved heat rays by wire gratings, 322.
- Rutherford (Prof. E.) on the production of helium by radium, 586; on the transformation and nomenclature of the radioactive emanations, 621.
- Sadler (Dr. C. A.) on the transformation of the energy of homogeneous Röntgen radiation into energy of corpuscular radiation, 447.
- Salts, on the positive ionization from hot, 669.
- Sangster (R. B.) on some consequences of Fresnel's reflexion of light theory, with formulæ for determining the angle of incidence in order to reflect  $1/n$ th the incident light, 305.
- Saturn's rings, on the origin of, 741; on the periodic times of, 949.
- Shaw (A. N.) on increased accuracy in the use of bifilar suspensions, 433.
- Shell, on the stresses in a heavy spherical, 191.
- Sherlock (R. L.) on the relationship of the Permian to the Trias in Nottinghamshire, 220.
- Shorter (S. A.) on the application of the theory of chemical potential to the thermodynamical theory of solutions, 933.
- Snow (E. C.) on the probability variations in distribution of  $\alpha$  particles, 198.
- Sodium, on the positive ionization from salts of, 669.
- Solutions, on a dynamical theory of, 17; on the application of the theory of chemical potential to the thermodynamical theory of, 933.
- Spectra, on the origin of, 214; on the, of the fluorescent Röntgen radiation, 396; on the resonance, of iodine vapour and their destruction by gases of the helium group, 469; on the, of the electrodeless ring discharge in certain gases, 720; on the separation of, in compound gases, 727; on a relation between the atomic volumes and the, of elements, 922.
- Spheres, on the initial accelerated motion of rigidly charged dielectric, 169; on Stokes's law for the motion of, through liquids, 755; on the motion of charged, 943.
- Spherical shell, on the stresses in a heavy, 191.
- Static charges, on lines of force due to given, 177.
- Stead (G.) on the separation of spectra in compound gases, 727.
- Stephenson (A.) on absorption and dispersion, 303.
- Stokes's law for the motion of spheres through liquids, on, 755.
- Stuhlmann (O.) on the difference in the photoelectric effect caused by incident and emergent light, 854.
- Suspensions, on bifilar, 433.
- Sutherland (W.) on weak electrolytes and towards a dynamical theory of solutions, 17.
- Swann (Dr. W. F. G.) on the magnetic field produced by a charged condenser moving through space, 150; on the longitudinal and transverse mass of an electron, 223.
- Temperature and molecular attraction, on the relation of, 84; on a thermostat for controlling the, of a room, 211.
- Tension and torsion, on a relation between, 740.
- Thermostat for controlling the temperature of a room, on a, 211.
- Thomas (H. H.) on the Skomer volcanic series, 465.
- Todd (G. W.) on the mobility of positive ions from heated aluminium phosphate in gases, 791.
- Tolman (Dr. R. C.) on non-Newtonian mechanics, 458.
- Townsend (Prof. J. S.) on charges on ions in gases, 204; on the mode of conduction in gases, 656, 816.
- Transformation and nomenclature of the radioactive emanations, on the, 621.
- Trowbridge (Prof. A.) on groove-form and energy distribution of diffraction gratings, 534.
- Ultra-violet light, on the intensity of the, emitted by an electrical discharge at low pressures, 412.

- Uranium, on the disintegration products of, 419.
- Vacuum valves, on electric, 1.
- Valency, on the question of, in gaseous ionization, 547.
- Vaporization of liquids, on the latent heat of, 263.
- Vincent (Dr. J. H.) on electrical experiments with mercury contained in tubes, 503.
- Wade (A.) on the eastern desert of Egypt, 467; on the rocks of north-eastern Montgomeryshire, 467.
- Wehnelt cathode, on rays of positive electricity from the, 926.
- Westphal (Dr. W.) on the question of valency in gaseous ionization, 547.
- Wheeler (Prof. L. F.) on the reflexion of light at certain metal-liquid surfaces, 229.
- Wilde (Dr. H.) on the origin of cometary bodies and Saturn's rings, 741; on the periodic times of Saturn's rings, 949.
- Wire gratings, on polarization of undiffracted long-waved heat rays by, 322.
- Wood (Prof. R.W.) on the resonance spectra of iodine vapour and their destruction by gases of the helium group, 469.
- X-rays, on the mode of ionization by, 222.
- Zinc, on the positive ionization from salts of, 669.

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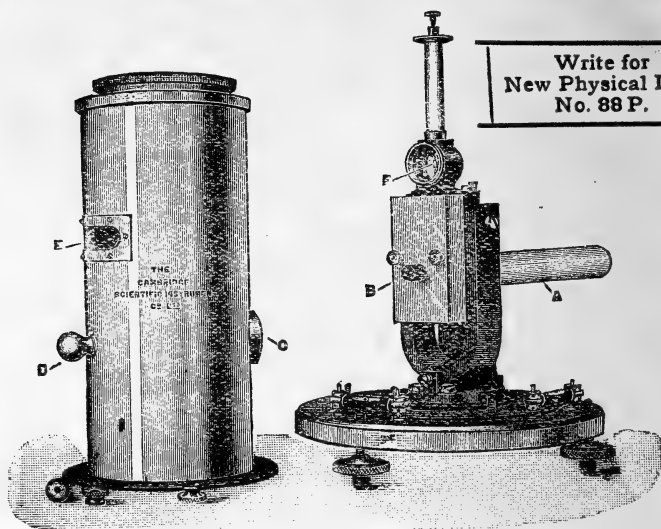
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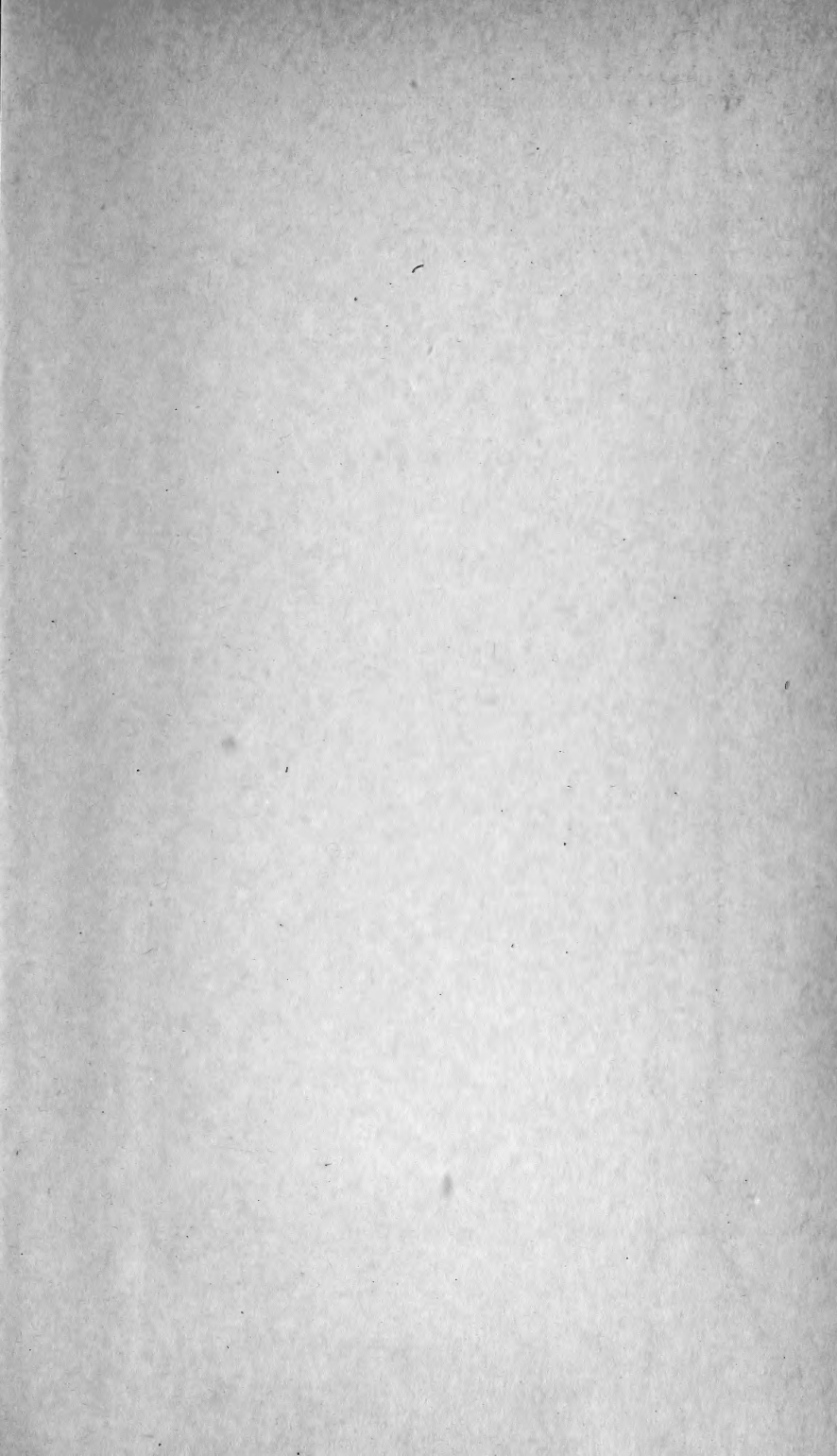
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## CONTENTS OF N° 131.—*Sixth Series.*

LXVI. The Positive Ionization from Hot Salts. By O. W. RICHARDSON, Professor of Physics, Princeton University . . . . .	page 669
LXVII. Note on the Diffusion of Neon through Hot Quartz. By O. W. RICHARDSON, Professor of Physics, and R. C. DITTO, Fellow in Physics, Princeton University . . . . .	704
LXVIII. The Induction-Coil. By E. TAYLOR JONES, D.Sc., Professor of Physics in the University College of North Wales, Bangor, and D. E. ROBERTS, B.Sc., Fellow of the University of Wales. (Plates XII. & XIII.) . . . . .	706
LXIX. On the Spectra of the Electrodeless Ring Discharge in certain Gases. By H. DONALDSON, B.A. (Camb.), B.Sc. (Lond.), Scholar of Sidney Sussex College, Cambridge . . . . .	720
LXX. On the Separation of Spectra in Compound Gases. By G. STEAD, B.A., formerly Scholar of Clare College, Cambridge . . . . .	727
LXXI. On the General Problem of Photographic Reproduction, with suggestions for enhancing Gradation originally invisible. By Lord RAYLEIGH, O.M., F.R.S. . . . .	734
LXXII. A Relation between Tension and Torsion. By R. A. HOUSTOUN, M.A., D.Sc., Ph.D., Lecturer on Physical Optics in the University of Glasgow . . . . .	740
LXXIII. On the Origin of Cometary Bodies and Saturn's Rings. By HENRY WILDE, D.Sc., D.C.L., F.R.S. (Plates XIV. & XV.) . . . . .	741
LXXIV. Limitations imposed by Slip and Inertia Terms upon Stokes's Law for the Motion of Spheres through Liquids. By H. D. ARNOLD, Fellow in Physics in the University of Chicago . . . . .	755
LXXV. The Mobility of the Positive Ion in Flames. By S. G. LUSBY, M.A. (Sydney), Emmanuel College, Cambridge, Barker Graduate Scholar of the University of Sydney . . . . .	775
LXXVI. The Mobility of Positive Ions produced from Heated Aluminium Phosphate in Gases at Low Pressures. By GEORGE W. TODD, M.Sc., B.A., 1851 Exhibition Scholar of Birmingham University; Emmanuel College, Cambridge . . . . .	791
LXXVII. The Radioactive Properties of High Temperature Flames. By H. CARTER, A.R.C.Sc., B.Sc., Royal College of Science, London . . . . .	805
LXXVIII. The Mode of Conduction in Gases. By Prof. JOHN S. TOWNSEND . . . . .	816
LXXIX. Notices respecting New Books :—Gesammelte Abhandlungen von FRIEDRICH KOHLRAUSCH; Dr. G. T. WALKER's Outlines of the Theory of Electromagnetism . . . . .	819
LXXX. Proceedings of Learned Societies :— GEOLOGICAL SOCIETY :—Dr. J. D. FALCONER on the Geology of Northern Nigeria . . . . .	820

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